# Why is Alkylation of an Enolate Accompanied by so Much Polyalkylation?

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**Supporting Information**

**Alkylation of α-Tetralone with Benzyl Bromide.** A preparative scale experiment was run by treating 0.93 g of α-tetralone in 14.7 g of THF with one equivalent of a solution of butyllithium in hexane. Two equivalents of benzyl bromide were added and stirred at room temperature. After 3 minutes an aliquot was quenched with isopropanol followed by water and extraction with methylene chloride. GC showed (without response corrections) a mono-/dialkylation ratio of 1.2/1. NMR analysis gave 90% α-tetralone and a mono-/di- ratio of 1.8. After complete reaction GC integration showed a di-/mono- ratio of >40/1.

**2-Benzyl-6-phenyl-α-tetralone (2).**[1] A mixture of 0.50 g (2.27 mmol) of 6-phenyl-1-tetralone and 4.5 mL of methyl magnesium carbonate (2.O M in DMF) in 20 mL of anhydrous DMF was heated under argon at 120-130 °C for 1 h, 0.5 mL (2.9 mmol) of benzyl bromide was added to the cooled solution and kept on the steam bath for 6 h. Flash column chromatography and sublimation gave 0.30 g (42%) a white solid, mp 113-4 °C; NMR (300 MHz, $CDCl_3$): 1.83 (m, 1H), 2.14 (m, 1H), 2.63-2.83 (m, 2H), 3.01 (m, 2H), 3.50 (dd, 1H), 7.2-7.6 (m, 12H), 8.13 (d, 1H); MS (m/Z), 312 ($M^+$), 284, 221, 165, 91; Anal: Calc. for $C_{23}H_{20}O$, C, 88.42; H, 6.45; Found: C, 88.24; H, 6.44.

**2,2-Dibenzyl-6-phenyl-α-tetralone (3)**. To a mixture of **2** and 1.1 equiv. of LDA in THF was added 2 equiv. of benzyl bromide. Flash column chromatography and recrystallization from ether/pentane gave a white solid, mp 145-6 °C; NMR

(300 MHz, $CDCl_3$) 8.16 (d, 1H), 7.60-7.14 (m, 17H), 3.35 (d, 2H), 3.10 (t, 2H), 2.67 (d, 2H), 1.96 (t, 2H); Anal: Calc. for $C_{30}H_{26}O$, C, 89.51, H, 6.51; found: C, 89.49, H, 6.43.

Table S1. Typical Lambert-Beers Law run (Run 818) for **1-Li**.(1 mm cell)

| {LiPAT}, M | $\lambda_{max}$, nm | Abs($\lambda_{max}$)/0.1 | Abs(367nm)/0.1 |
|---|---|---|---|
| 0.0014350 | 337.5 | 16.521 | 8.5890 |
| 0.0012040 | 338.0 | 13.712 | 7.2290 |
| 0.00096690 | 337.5 | 10.978 | 5.8340 |
| 0.00084190 | 338.0 | 9.517 | 5.0480 |
| 0.00074960 | 337.5 | 8.467 | 4.5030 |
| 0.00067440 | 337.0 | 7.613 | 4.0660 |
| 0.00060390 | 337.5 | 6.818 | 3.6580 |
| 0.00054800 | 337.5 | 6.152 | 3.2880 |
| 0.00049890 | 337.0 | 5.604 | 2.9960 |
| 0.00046040 | 337.5 | 5.144 | 2.7770 |
| 0.00041550 | 337.5 | 4.661 | 2.5070 |
| 0.00038570 | 338.0 | 4.309 | 2.3260 |
| 0.00036010 | 337.5 | 4.032 | 2.1860 |
| 0.00033600 | 337.5 | 3.766 | 2.0340 |
| 0.00031120 | 338.0 | 3.484 | 1.8880 |
| 0.00028500 | 338.0 | 3.200 | 1.7300 |
| 0.00025350 | 336.5 | 2.826 | 1.5500 |
| 0.00021740 | 337.0 | 2.412 | 1.3180 |
| 0.00018600 | 337.5 | 2.056 | 1.1200 |
| 0.00016440 | 338.5 | 1.842 | 1.0170 |
| 0.00012860 | 338.5 | 1.436 | 0.7840 |

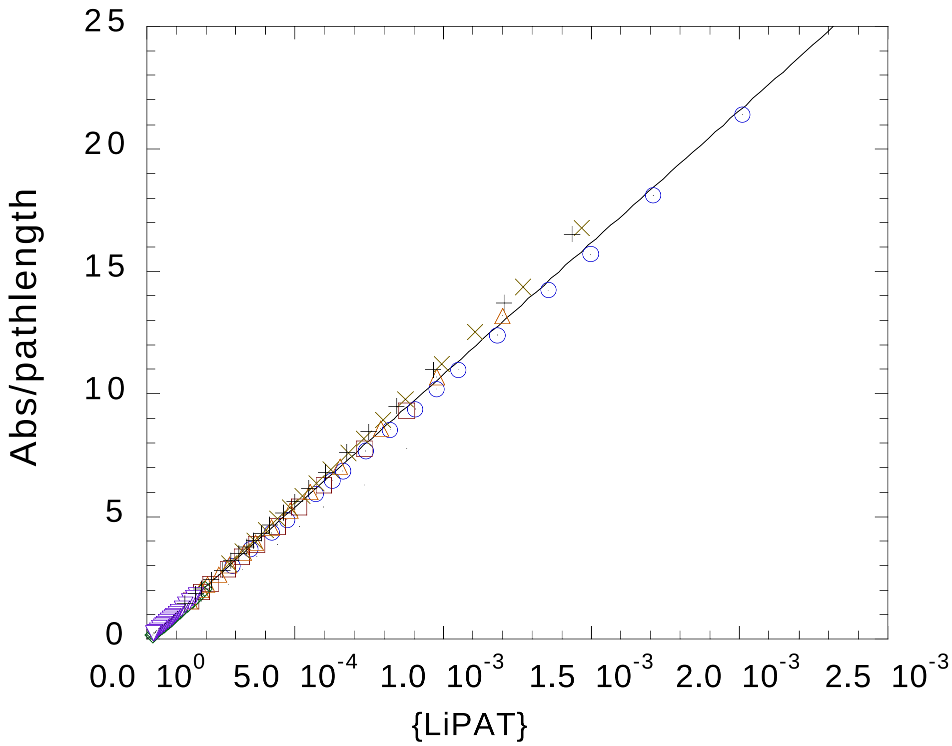


Fig. S1. Plot of absorbance in THF at 25 °C at $\lambda_{max}$ vs {LiPAT}, the formal concentration of **1-Li** for seven runs; the slope of the line shown is 10784 ± 57, $R^2$ = 0.993.

Table S2. Spectral data for LiBnPAT in THF at 25 °C.

| {LiBnPAT} (M) | $\lambda$max (nm) | Absorbance at 361.0 nm | Absorbance at $\lambda_{max}$ |
|---|---|---|---|
| Series 1 | 1 mm cell | | |
| 0.001687 | 359.5 | 2.1985 | 2.2039 |
| 0.0013755 | 359 | 1.7604 | 1.7692 |
| 0.0011921 | 359.5 | 1.5219 | 1.5225 |
| 0.0010348 | 360 | 1.315 | 1.3159 |
| 0.0009123 | 360.5 | 1.1568 | 1.1571 |
| 0.0008136 | 361 | 1.0279 | 1.0279 |
| 0.0007051 | 362 | 0.8886 | 0.889 |
| 0.0006183 | 363 | 0.7745 | 0.7757 |
| 0.0005412 | 359.5 | 0.6763 | 0.6766 |
| 0.0004741 | 362 | 0.5893 | 0.5896 |
| 0.0004132 | 363 | 0.512 | 0.5135 |
| 0.0003607 | 361.5 | 0.4507 | 0.4507 |
| Series 2 | 1 cm cell | | |
| 0.0001373 | 362.5 | 1.689 | 1.6912 |
| 0.0001262 | 362.5 | 1.574 | 1.5794 |
| 0.0001081 | 362.5 | 1.314 | 1.3208 |

| | | | |
|---|---|---|---|
| 0.0001015 | 362.5 | 1.232 | 1.2398 |
| 0.0000867 | 362.5 | 1.044 | 1.0509 |

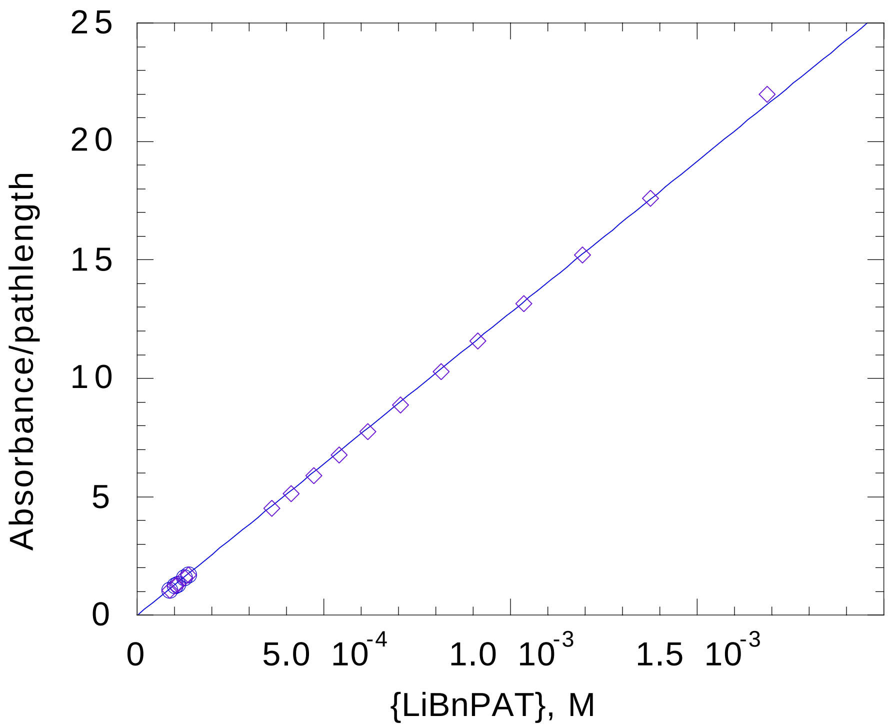


Fig. S2. Plot of absorbance in THF at 25 °C for 1 cm cell vs {LiBnPAT}, the formal concentration of **2-Li** for two runs; the slope of the line shown is 12779 ± 46, $R^2 = 0.999$.

Table S3. Ion pair acidity experiments with LiPAT and either Ph3,4-BF

| {LiPAT}, M | {LiPh34BF}, M | [PAT], M | [Ph-3,4-BF] M | Kcorr | $pK_{ob}$ | {LiPAT}/Kcorr |
|---|---|---|---|---|---|---|
| Run 1 | | | | | | |
| 1.71E-04 | 5.95E-05 | 5.12E-03 | 7.44E-03 | 6.288 | 14.08 | 2.72E-05 |
| 1.94E-04 | 6.55E-05 | 5.10E-03 | 7.43E-03 | 6.365 | 14.08 | 3.05E-05 |
| 4.27E-04 | 9.04E-05 | 4.86E-03 | 7.41E-03 | 10.01 | 13.88 | 4.26E-05 |
| 6.05E-04 | 1.06E-04 | 4.69E-03 | 7.39E-03 | 12.25 | 13.79 | 4.94E-05 |
| 8.33E-04 | 1.20E-04 | 4.46E-03 | 7.38E-03 | 15.33 | 13.69 | 5.44E-05 |
| 1.37E-03 | 1.53E-04 | 3.92E-03 | 7.34E-03 | 21.67 | 13.54 | 6.33E-05 |
| 1.62E-03 | 1.67E-04 | 3.67E-03 | 7.33E-03 | 24.74 | 13.49 | 6.55E-05 |
| Run 2 | | | | | | |
| 1.18E-04 | 7.98E-05 | 3.31E-03 | 7.29E-03 | 4.624 | 14.21 | 2.55E-05 |
| 1.75E-04 | 9.42E-05 | 3.25E-03 | 7.28E-03 | 5.735 | 14.12 | 3.05E-05 |
| 2.17E-04 | 1.04E-04 | 3.21E-03 | 7.27E-03 | 6.422 | 14.07 | 3.39E-05 |
| 2.77E-04 | 1.15E-04 | 3.15E-03 | 7.26E-03 | 7.396 | 14.01 | 3.74E-05 |
| 3.49E-04 | 1.26E-04 | 3.08E-03 | 7.25E-03 | 8.618 | 13.94 | 4.04E-05 |
| 4.10E-04 | 1.37E-04 | 3.02E-03 | 7.24E-03 | 9.367 | 13.91 | 4.38E-05 |
| 4.72E-04 | 1.47E-04 | 2.96E-03 | 7.23E-03 | 10.17 | 13.87 | 4.64E-05 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5.46E-04 | 1.57E-04 | 2.88E-03 | 7.22E-03 | 11.22 | 13.83 | 4.87E-05 |
| 6.07E-04 | 1.65E-04 | 2.82E-03 | 7.21E-03 | 12.04 | 13.8 | 5.05E-05 |
| 6.63E-04 | 1.73E-04 | 2.77E-03 | 7.20E-03 | 12.73 | 13.78 | 5.21E-05 |
| 7.33E-04 | 1.81E-04 | 2.70E-03 | 7.19E-03 | 13.66 | 13.74 | 5.37E-05 |
| 8.18E-04 | 1.94E-04 | 2.61E-03 | 7.18E-03 | 14.55 | 13.72 | 5.62E-05 |
| 8.60E-04 | 1.98E-04 | 2.57E-03 | 7.17E-03 | 15.19 | 13.7 | 5.66E-05 |
| Run 3 | | | | | | |
| 5.50E-05 | 3.39E-05 | 4.37E-03 | 7.41E-03 | 4.713 | 14.21 | 1.17E-05 |
| 9.56E-05 | 5.04E-05 | 4.33E-03 | 7.39E-03 | 5.036 | 14.18 | 1.90E-05 |
| 1.39E-04 | 6.20E-05 | 4.29E-03 | 7.38E-03 | 5.77 | 14.12 | 2.41E-05 |
| 1.96E-04 | 7.29E-05 | 4.23E-03 | 7.37E-03 | 6.75 | 14.05 | 2.90E-05 |
| 2.57E-04 | 8.29E-05 | 4.17E-03 | 7.36E-03 | 7.729 | 13.99 | 3.32E-05 |
| 3.15E-04 | 9.10E-05 | 4.11E-03 | 7.35E-03 | 8.616 | 13.94 | 3.66E-05 |
| 3.70E-04 | 1.00E-04 | 4.05E-03 | 7.34E-03 | 9.158 | 13.92 | 4.05E-05 |
| 4.60E-04 | 1.09E-04 | 3.96E-03 | 7.33E-03 | 10.59 | 13.86 | 4.34E-05 |
| 5.44E-04 | 1.16E-04 | 3.88E-03 | 7.33E-03 | 11.84 | 13.81 | 4.60E-05 |
| 6.69E-04 | 1.26E-04 | 3.76E-03 | 7.32E-03 | 13.68 | 13.74 | 4.89E-05 |
| 7.86E-04 | 1.36E-04 | 3.64E-03 | 7.31E-03 | 15.21 | 13.7 | 5.17E-05 |
| 8.94E-04 | 1.45E-04 | 3.53E-03 | 7.30E-03 | 16.54 | 13.66 | 5.41E-05 |
| Run 4 | | | | | | |
| {LiPAT}, M[a] | {LiTPI}, M | [PAT], M | [TPI], M | Kcorr | $pK_{ob}$ | {LiPAT}/Kcorr |
| 5.44E-05 | 3.09E-05 | 4.59E-03 | 7.05E-03 | 4.746 | 14.29 | 1.15E-05 |
| 1.05E-04 | 5.06E-05 | 4.54E-03 | 7.03E-03 | 5.003 | 14.27 | 2.11E-05 |
| 1.54E-04 | 5.96E-05 | 4.49E-03 | 7.02E-03 | 6.048 | 14.19 | 2.54E-05 |
| 2.16E-04 | 6.99E-05 | 4.43E-03 | 7.01E-03 | 7.111 | 14.12 | 3.03E-05 |
| 3.25E-04 | 8.02E-05 | 4.32E-03 | 7.00E-03 | 9.312 | 14 | 3.49E-05 |
| 4.29E-04 | 8.78E-05 | 4.22E-03 | 6.99E-03 | 11.31 | 13.92 | 3.79E-05 |
| 5.33E-04 | 9.76E-05 | 4.11E-03 | 6.98E-03 | 12.75 | 13.86 | 4.18E-05 |
| 6.76E-04 | 1.06E-04 | 3.97E-03 | 6.97E-03 | 15.13 | 13.79 | 4.47E-05 |
| 8.15E-04 | 1.17E-04 | 3.83E-03 | 6.96E-03 | 16.86 | 13.74 | 4.83E-05 |
| 9.77E-04 | 1.30E-04 | 3.67E-03 | 6.95E-03 | 18.68 | 13.7 | 5.23E-05 |
| 1.13E-03 | 1.41E-04 | 3.52E-03 | 6.94E-03 | 20.57 | 13.66 | 5.47E-05 |

(a) Neutral TPI has strong absorption below 360.0 nm, therefore, the abso
6340) was used to obtain the concentration of {LiPAT}.

Table S4. Ion pair acidity experiments with LiBnPAT (2a) and TeFPFl.

| {LiBnPAT, M | {LiTeFPFl}, M | [BnPAT], M | [TeFPFl] M | Kcorr | $pK_{ob}$ | {LiBnPAT}/Kcorr |
|---|---|---|---|---|---|---|
| 8.44E-04 | 6.50E-04 | 4.12E-03 | 1.90E-02 | 5.54 | 13.377 | 1.53E-04 |
| 6.43E-04 | 5.26E-04 | 4.37E-03 | 1.92E-02 | 5.02 | 13.419 | 1.28E-04 |
| 6.31E-04 | 5.13E-04 | 4.39E-03 | 1.92E-02 | 5.03 | 13.419 | 1.25E-04 |
| 6.09E-04 | 4.99E-04 | 4.41E-03 | 1.92E-02 | 4.98 | 13.423 | 1.22E-04 |
| 3.25E-04 | 3.29E-04 | 3.88E-03 | 1.60E-02 | 3.87 | 13.532 | 8.39E-05 |
| 2.62E-04 | 2.75E-04 | 3.97E-03 | 1.61E-02 | 3.69 | 13.553 | 7.10E-05 |
| 1.42E-04 | 1.79E-04 | 3.14E-03 | 1.25E-02 | 3.02 | 13.641 | 4.70E-05 |
| 1.30E-04 | 1.67E-04 | 3.16E-03 | 1.25E-02 | 2.97 | 13.648 | 4.38E-05 |
| 1.46E-03 | 3.84E-04 | 1.94E-03 | 4.07E-03 | 7.25 | 13.260 | 2.02E-04 |
| 1.10E-03 | 3.12E-04 | 1.74E-03 | 3.39E-03 | 6.27 | 13.323 | 1.75E-04 |
| 1.01E-03 | 2.91E-04 | 1.83E-03 | 3.42E-03 | 5.97 | 13.344 | 1.69E-04 |
| 9.82E-04 | 2.82E-04 | 1.86E-03 | 3.42E-03 | 5.91 | 13.348 | 1.66E-04 |
| 9.71E-04 | 2.82E-04 | 1.87E-03 | 3.42E-03 | 5.82 | 13.355 | 1.67E-04 |

Table S5. Initial rates of reaction of **1-Li** with benzyl bromide at 25 °C in THF; [BnBr] = 0.02073M.

| {**1-Li**}, M | rate, M $s^{-1}$ | [M], M | [T], M |
|---|---|---|---|
| 4.13E-04 | 3.80E-07 | 1.86E-04 | 5.67E-05 |
| 6.42E-04 | 4.15E-07 | 2.18E-04 | 1.06E-04 |
| 8.15E-04 | 4.61E-07 | 2.36E-04 | 1.46E-04 |
| 1.10E-03 | 5.09E-07 | 2.59E-04 | 2.11E-04 |
| 2.03E-04 | 3.07E-07 | 1.37E-04 | 1.66E-05 |
| 4.94E-04 | 3.92E-07 | 1.99E-04 | 7.37E-05 |
| 7.46E-04 | 4.38E-07 | 2.29E-04 | 1.27E-04 |
| 9.65E-04 | 4.97E-07 | 2.49E-04 | 1.79E-04 |
| 1.19E-03 | 4.86E-07 | 2.65E-04 | 2.32E-04 |
| 1.76E-03 | 5.89E-07 | 2.97E-04 | 3.66E-04 |
| 1.31E-03 | 5.26E-07 | 2.72E-04 | 2.57E-04 |
| 4.07E-04 | 3.86E-07 | 1.86E-04 | 5.56E-05 |
| 7.36E-04 | 4.32E-07 | 2.28E-04 | 1.27E-04 |

Table S6. Initial rates of reaction of **2-Li** with benzyl bromide at 25 ℃ in THF; [BnBr] = 0.01542M.

| {**2-Li**}, M | rate, M $s^{-1}$ | [M], M | [D], M |
|---|---|---|---|
| 1.42E-03 | 1.03E-06 | 3.72E-04 | 5.25E-04 |
| 9.49E-04 | 8.52E-07 | 2.94E-04 | 3.27E-04 |
| 1.26E-03 | 8.45E-07 | 3.47E-04 | 4.57E-04 |
| 3.34E-04 | 4.00E-07 | 1.54E-04 | 9.02E-05 |
| 7.12E-04 | 6.73E-07 | 2.47E-04 | 2.32E-04 |
| 1.12E-03 | 8.46E-07 | 3.24E-04 | 3.99E-04 |
| 5.75E-04 | 5.93E-07 | 2.17E-04 | 1.79E-04 |
| 5.01E-04 | 5.08E-07 | 1.99E-04 | 1.51E-04 |
| 9.92E-04 | 8.27E-07 | 3.01E-04 | 3.45E-04 |

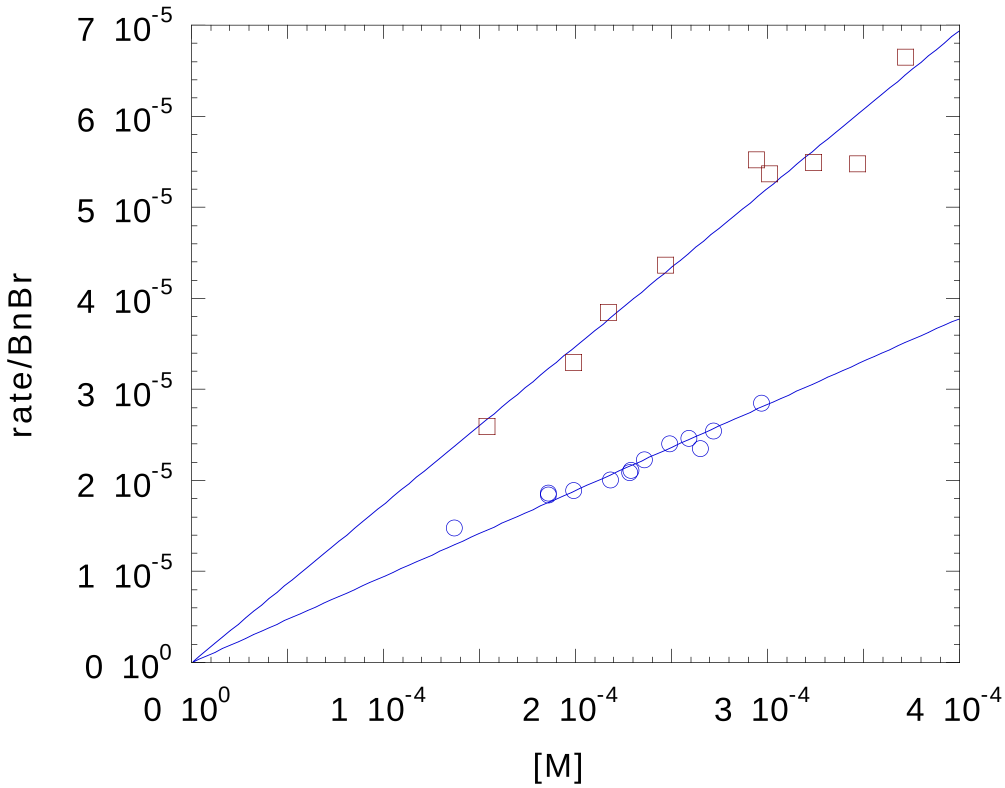


Figure S3. Plots of rate/[BnBr] for reactions of **1-Li** (circles) and **2-Li** (squares) vs monomer concentration. Slopes of lines through the origin are 0.0945 ± 0.0010 and 0.174 ± 0.003, respectively.

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[1] Preparation by Kai-Cha Feng.