# Tuning the depth of bowl-shaped phosphine hosts: capsule and cage architectures in host-guest complexes with $\mathbf{C}_{60}$ fullerene 

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## (1) General methods

All chemicals were reagent grade, and used without further purification. All reactions were performed under a nitrogen atmosphere. Racemic mixture, $P$-isomer, and $M$-isomer of $\mathbf{1}$ were synthesized according to literature procedure. Chromatography was performed using $\mathrm{SiO}_{2}-60 \mathrm{~N}$ ( $0.063-0.212 \mathrm{~mm}$; Kanto). A recycling preparative HPLC was performed using a JAI LC-908 equipped with JAIGEL-1H and -2 H columns (GPC) using $\mathrm{CHCl}_{3}$ as an eluent. A preparative chiral resolution was performed using a JAI LC-9201 equipped with a DAICEL CHIRALPAK IA columns using 1:4 hexane/ $\mathrm{CHCl}_{3}$ as an eluent. Melting points were determined using a Yanaco melting point apparatus and are uncorrected. The ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{31} \mathrm{P}$ NMR spectra were recorded by Bruker AVANCE400 ( 400 MHz ) spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Aldrich and used as received. In the NMR measurements, tetramethylsilane was used as the internal standard $(0 \mathrm{ppm})$ for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR and phosphorous acid was used as the external standard ( 0 ppm ) for ${ }^{31} \mathrm{P}$ NMR. MALDI-TOF mass spectra were recorded by an AB Sciex TOF/TOF5800. UV-vis absorption spectra were recorded by JASCO Ubest V-660. Circular dichroism spectra were recorded by a JASCO J-720W. Specific rotation ([ $\square]_{\mathrm{D}}$ ) was measured at 17 ${ }^{\circ} \mathrm{C}$ in chloroform by a JASCO DIP-1000.

## (2) Synthetic procedure

## Synthesis of phosphine sulfide 2

To a toluene solution ( 3 mL ) of ( rac ) $\mathbf{- 1}(20.1 \mathrm{mg}, 32.4 \mu \mathrm{~mol})$ was added Lawesson's reagent (11.2 $\mathrm{mg}, 27.7 \mu \mathrm{~mol})$ and then the mixture was refluxed for 12 hours. The reaction mixture was separated by silica-gel column chromatography to give colorless powder of ( rac ) $\mathbf{- 2}$ ( $20.3 \mathrm{mg}, 31.9 \mu \mathrm{~mol}, 98 \%$ ). Enantiopure $(M) \mathbf{- 2}$ and $(P) \mathbf{- 2}$ were prepared from $(M) \mathbf{- 1}$ and $(P) \mathbf{- 1}$ in $86 \%$ and $93 \%$ yield, respectively.
2: colorless powder, $\mathrm{mp}>300{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta \square 7.30 \square \square \mathrm{dd}, J=8.8 \square \square 4.8 \mathrm{~Hz}$, $3 \mathrm{H}), 7.39-7.41(\mathrm{~m}, 9 \mathrm{H}), 7.60-7.63(\mathrm{~m}, 6 \mathrm{H}), 7.65(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \square 82.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=2.0 \mathrm{~Hz}\right), 95.7,110.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=85.1 \mathrm{~Hz}\right), 111.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=6.8 \mathrm{~Hz}\right), 116.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=5.9\right.$ Hz ), 122.7, 128.4, 128.9, 131.8, 136.2, 157.9, 158.0; ${ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta \square-$ 52.2 $\square \square$ MALDI-TOF MS $m / z 637.17[\mathbf{2}+\mathrm{H}]^{+}$; Anal. Calcd for $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{PS} \cdot \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 77.05 ; \mathrm{H}, 3.54$. Found: C, $76.87 ; \mathrm{H}, 3.74 ;[\alpha]_{\mathrm{D}}$ for $M-2:+1132\left(\mathrm{CHCl}_{3}, c=0.078,17^{\circ} \mathrm{C}\right)$.

To a toluene solution ( 5 mL ) of ( rac ) $\mathbf{- 2}(16.0 \mathrm{mg}, 25.1 \mu \mathrm{~mol})$ was added hexamethylphosphorus triamide $(10 \mu \mathrm{~L}, 55 \mu \mathrm{~mol})$ and then the mixture was refluxed for 24 hours. The reaction mixture was separated by silica-gel column chromatography to give colorless powder of (rac)-3 ( $10.7 \mathrm{mg}, 17.7$ $\mu \mathrm{mol}, 70 \%$ ). Enantiopure $(M) \mathbf{- 3}$ and $(P)$ - $\mathbf{3}$ were prepared from $(M) \mathbf{- 2}$ and $(P) \mathbf{- 2}$ in $88 \%$ and $97 \%$ yield, respectively.
3: colorless powder, $\operatorname{mp} 234{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.16(\mathrm{dd}, J=8.4,1.6 \mathrm{~Hz}, 3 \mathrm{H}), 7.36-$ $7.40(\mathrm{~m}, 9 \mathrm{H}), 7.49(\mathrm{dd}, J=8.4,1.6 \mathrm{~Hz}, 3 \mathrm{H}), 7.58-7.62(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 83.4$, $94.5,111.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=1.8 \mathrm{~Hz}\right), 113.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=15 \mathrm{~Hz}\right), 115.4,123.2,128.4,128.5,131.7,133.6,155.3$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{P}}=6.8 \mathrm{~Hz}\right), 155.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{P}}=6.6 \mathrm{~Hz}\right) ;{ }^{31} \mathrm{P}$ NMR $\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta-132.3$; MALDI-TOF MS $m / z 604.14$ [M]; Anal. Calcd for $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{P} \cdot 0.2 \mathrm{H}_{2} \mathrm{O}: \mathrm{C}, 82.94 ; \mathrm{H}, 3.55$. Found: C, 82.90; H, 3.95; $[\alpha]_{\mathrm{D}}$ for $P-3:-1751\left(\mathrm{CHCl}_{3}, c=0.083,17^{\circ} \mathrm{C}\right)$.
(3) NMR spectra


Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathrm{rac}) \mathbf{- 2}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$.


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectrum of (rac)-2 $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


Figure S3. ${ }^{31} \mathrm{P}$ NMR spectrum of (rac)-2 $\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


Figure S4. ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathrm{rac}) \mathbf{- 3}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


Figure S5. ${ }^{13} \mathrm{C}$ NMR spectrum of (rac)-3 ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


Figure S6. ${ }^{31} \mathrm{P}$ NMR spectrum of (rac)-3 ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
(4) UV-vis absorption and circular dichroism spectra


Figure S7. UV-vis absorption (bottom) and CD (top) spectra of ( $P$ )- (red) and ( $M$ )-2 (black) in chloroform.


Figure S8. UV-vis absorption (bottom) and CD (top) spectra of $(P)$ - (red) and ( $M$ )-3 (black) in chloroform.

## (5) MALDI-TOF MS



Figure S9. MALDI-TOF MS (negative) of $[(P)-\mathbf{2}]_{4} \supset \mathrm{C}_{60}$. Inset shows ion peas for $\left[\mathbf{2} \supset \mathrm{C}_{60}\right]^{-}$with isotope simulation.


Figure S10. MALDI-TOF MS (negative) of $[(M)-3][(P)-3] \supset \mathrm{C}_{60}$. Insets show ion peas for $\left[3 \supset \mathrm{C}_{60}\right]^{-}$ and $\left[(3)_{2} \supset \mathrm{C}_{60}\right]^{-}$with isotope simulation.

## (6) X-ray crystallographic analysis

X-ray diffraction measurements were performed using a Bruker APEXII ULTRA. The X-ray diffraction intensities were collected on a CCD diffractometer at 120 K using $\mathrm{MoK} \alpha$ (graphitemonochromated, $\lambda=0.71073 \AA$ ) radiation. The data were integrated with SAINT (Bruker, 2004), and an empirical absorption correction (SADABS) was applied. The structure was solved by the direct method of SHELXS-97 or SHELXD-2014 and refined using the SHELXL-97 or SHELXL2014 program. ${ }^{1,2}$ All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^{2}$ by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and refined riding on their corresponding carbon atoms. The crystallographic data for $(\mathrm{rac}) \mathbf{- 2},(M) \mathbf{2},(\mathrm{rac}) \mathbf{- 3},(M) \mathbf{3},[(P)-\mathbf{2}]_{4} \supset \mathrm{C}_{60}$, and $[(M)-\mathbf{3}][(P)-\mathbf{3}] \supset \mathrm{C}_{60}$ were deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1060806-1060809, 1060816, and 1060817. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; email: deposit $@$,ccdc.cam.ac.uk).



Figure S11. ORTEP drawing of (rac)-2, top (left) and side (right) views; thermal ellipsoids set at $50 \%$ probability. One of the enantiomers is shown.


Figure S13. ORTEP drawing of ( $M$ )-2, top (left) and side (right) views; thermal ellipsoids set at $50 \%$ probability.



Figure S12. ORTEP drawing of (rac)-3, top (left) and side (right) views; thermal ellipsoids set at $50 \%$ probability. One of the enantiomers is shown.



Figure S14. ORTEP drawing of $(M)$-3, top (left) and side (right) views; thermal ellipsoids set at $50 \%$ probability.


Figure S15. ORTEP drawing of $[(M)-3][(P)-3] \supset \mathrm{C}_{60}$, top (left) and side (right) views; thermal ellipsoids set at $50 \%$ probability.


Figure S16. ORTEP drawing of $[(P)-\mathbf{2}]_{4} \supset \mathrm{C}_{60}$; thermal ellipsoids set at $50 \%$ probability.

Table S1. Crystallographic data.

|  | (rac)-2 | (M)-2 | $[(P)-\mathbf{2}]_{4} \supset \mathrm{C}_{60}$ |
| :---: | :---: | :---: | :---: |
| Composite | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{PS} \cdot \mathrm{CHCl}_{3}$ | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{PS}$ | $\begin{aligned} & \left(\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{PS}\right)_{4} \cdot \mathrm{C}_{60} \\ & \cdot\left(\mathrm{CHCl}_{3}\right)_{3} \end{aligned}$ |
| Formula | $\mathrm{C}_{43} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{PSCl}_{3}$ | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{PS}$ | $\mathrm{C}_{231} \mathrm{H}_{87} \mathrm{O}_{12} \mathrm{P}_{4} \mathrm{~S}_{4} \mathrm{Cl}_{9}$ |
| Formula weight | 755.98 | 636.62 | 3625.17 |
| Crystal size ( $\mathrm{mm}^{3}$ ) | $0.20 \times 0.05 \times 0.02$ | $0.20 \times 0.10 \times 0.05$ | $0.20 \times 0.02 \times 0.01$ |
| Crystal system | monoclinic | monoclinic | tetragonal |
| Space group | $P 2{ }_{1} / n$ | $P 2_{1}$ | P41 |
| $a(\AA)$ | 14.036(5) | 10.913(3) | 31.8140(15) |
| $b(\AA)$ | 16.260(6) | 16.970(4) | 31.8140(15) |
| $c(\AA)$ | 16.551(6) | 17.246(4) | 16.4344(9) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 109.896(3) | 100.936(3) | 90 |
| $\gamma(\mathrm{deg})$ | 90 | 90 | 90 |
| $V\left(\AA^{3}\right)$ | 3552(2) | 3135.8(13) | 16633.8(18) |
| Z | 4 | 4 | 4 |
| $D_{\text {calcd }}\left(\mathrm{g} \cdot \mathrm{cm}^{-3}\right)$ | 1.414 | 1.348 | 1.448 |
| Collected/Unique | 33137/7145 | 34659/14143 | 144715/24006 |
| $R_{\text {int }}$ | 0.0681 | 0.0557 | 0.1100 |
| $\theta_{\text {max }}(\mathrm{deg})$ | 26.34 | 27.61 | 23.32 |
| $F_{000}$ | 1544 | 1312 | 7384 |
| $\mu(\mathrm{MoK} \alpha)\left(\mathrm{mm}^{-1}\right)$ | 0.403 | 0.196 | 0.312 |
| Limiting indices | $-17 \leq h \leq 16$ | $-14 \leq h \leq 14$ | $-29 \leq h \leq 35$ |
|  | $-20 \leq k \leq 20$ | $-22 \leq k \leq 21$ | $-34 \leq k \leq 35$ |
|  | $-18 \leq l \leq 20$ | $-22 \leq l \leq 22$ | $-18 \leq l \leq 18$ |
| Parameters/restraints | 481/0 | 847/0 | 2341/1 |
| Goodness of fit ( $F^{2}$ ) | 0.987 | 1.032 | 1.147 |
| $R_{1}(I>2 \sigma(I))$ | 0.0924 | 0.0501 | 0.1104 |
| $w R_{2}$ (all date) | 0.2138 | 0.1086 | 0.2503 |
|  | - | -0.04(6) | 0.16(3) |


|  | ( rac ) $\mathbf{3}$ | (M)-3 | $[(M)-3][(P)-3] \supset \mathrm{C}_{60}$ |
| :---: | :---: | :---: | :---: |
| Composite | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{P} \cdot \mathrm{H}_{2} \mathrm{O}$ | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{P}$ | $\left(\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{P}\right)_{2} \cdot \mathrm{C}_{60}$ |
| Formula | $\mathrm{C}_{42} \mathrm{H}_{23} \mathrm{O}_{4} \mathrm{P}$ | $\mathrm{C}_{42} \mathrm{H}_{21} \mathrm{O}_{3} \mathrm{P}$ | $\mathrm{C}_{144} \mathrm{H}_{42} \mathrm{O}_{6} \mathrm{P}_{2}$ |
| Formula weight | 622.57 | 604.56 | 1929.71 |
| Crystal size ( $\mathrm{mm}^{3}$ ) | $0.10 \times 0.03 \times 0.03$ | $0.40 \times 0.01 \times 0.01$ | $0.05 \times 0.05 \times 0.05$ |
| Crystal system | trigonal | orthorhombic | trigonal |
| Space group | $P-3$ | $P 22_{12} 2$ | R-3 |
| $a(\AA)$ | 20.785(7) | 30.262(14) | 19.058(12) |
| $b(\AA)$ | 20.785(7) | 51.48(2) | 19.058(12) |
| $c(\AA)$ | 4.1189(15) | 4.0818(19) | 20.787(14) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 90 | 90 | 90 |
| $\gamma$ (deg) | 120 | 90 | 120 |
| $V\left(\AA^{3}\right)$ | 1541.1(11) | 6359(5) | 6539(9) |
| Z | 2 | 8 | 3 |
| $D_{\text {calcd }}\left(\mathrm{g} \cdot \mathrm{cm}^{-3}\right)$ | 1.342 | 1.263 | 1.470 |
| Collected/Unique | 8681/2351 | 33744/9120 | 11604/3025 |
| $R_{\text {int }}$ | 0.0331 | 0.1595 | 0.0926 |
| $\theta_{\text {max }}(\mathrm{deg})$ | 27.51 | 23.23 | 26.50 |
| $F_{000}$ | 644 | 2496 | 2952 |
| $\mu(\mathrm{MoK} \alpha)\left(\mathrm{mm}^{-1}\right)$ | 0.135 | 0.126 | 0.124 |
| Limiting indices | $-27 \leq h \leq 26$ | $-33 \leq h \leq 32$ | $-23 \leq h \leq 18$ |
|  | $-22 \leq k \leq 27$ | $-55 \leq k \leq 57$ | $-23 \leq k \leq 23$ |
|  | $-5 \leq l \leq 4$ | $-4 \leq l \leq 4$ | $-24 \leq l \leq 26$ |
| Parameters/restraints | 143/0 | 819/0 | 229/0 |
| Goodness of fit ( $F^{2}$ ) | 1.084 | 1.084 | 1.097 |
| $R_{1}(I>2 \sigma(l))$ | 0.0523 | 0.0901 | 0.0498 |
| $w R_{2}$ (all date) | 0.1255 | 0.1854 | 0.1198 |
|  | - | -0.09(16) | - |

## (7) Computational methods.

All computations were performed using the Gaussian09 packages ${ }^{3}$ with the M06-2X functional. ${ }^{4}$ The basis set $6-31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ was used for the geometry optimizations and NBO analysis, and timedependent calculations.

Table S2. Comparison of experimental and calculated structure parameters of 1-3.

|  |  | 1 | 2 |  | 3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| P-X bond length/ $\AA$ | $\exp (r a c)$ | 1.475(3) | 1.929(2) | - |  |
|  | exp (chiral) | 1.466(4) | 1.928(2) | - |  |
|  | calc | 1.485 | 1.939 | - |  |
| $\mathrm{C}-\mathrm{P}-\mathrm{X}$ bond angles/deg | $\exp (r a c)$ | 119.2 | 120.0 | - |  |
|  | exp (chiral) | 119.0 | 119.6 | - |  |
|  | calc | 120.1 | 120.4 | - |  |
| $\mathrm{C}-\mathrm{P}-\mathrm{C}$ bond angles/deg ${ }^{a}$ | exp (rac) | 98.3 | 97.1 | 93.8 |  |
|  | $\exp$ (chiral) | 98.4 | 97.7 | 94.0 |  |
|  | calc | 97.1 | 96.7 | 92.4 |  |
| Bowl depth $/ \AA$ ( height) ${ }^{b}$ | $\exp (r a c)$ | 2.089 | 2.183 | 2.400 |  |
|  | $\exp$ (chiral) | 2.087 | 2.112 | 2.453 |  |
|  | calc | 2.215 | 2.232 | 2.463 |  |
| Bowl depth $/ \AA$ (center) ${ }^{c}$ | $\exp (r a c)$ | 2.089 | 2.184 | 2.400 |  |
|  | exp (chiral) | 2.087 | 2.112 | 2.453 |  |
|  | calc | 2.215 | 2.232 | 2.463 |  |
| Generatrix length/ $\AA^{d}$ | $\exp$ (rac) | 4.44 | 4.47 | 4.537 |  |
|  | exp (chiral) | 4.47 | 4.47 | 4.54 |  |
|  | calc | 4.505 | 4.509 | 4.570 |  |

$a 2 \times \angle \mathrm{C}-\mathrm{P}-\mathrm{Y}$ (Y: the centroid of the plane consisting of the three terminal carbon atoms); $b$ a height from the bottom to the P atom; $c$ distance between the P atom and the center of the bottom plane; $d$ an averaged distance between the P atom and the terminal carbon atom.



Table S3. Singlet electronic excitation of $(M) \mathbf{- 1},(M) \mathbf{- 2}$, and $(M) \mathbf{- 3}$ based on TD DFT calculation.

|  | excited state | wave function $^{a}$ | $\lambda / \mathrm{nm}$ | $f$ | $R / 10^{-40} \mathrm{cgs}$ <br> (velocity) |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{S}_{1}(\mathrm{E})$ | $0.50 \times \mathrm{H}-1 \rightarrow \mathrm{~L}$ | 297 | 1.267 | 541.23 |
| $(M) \mathbf{- 1}$ | $\mathrm{S}_{2}(\mathrm{E})$ | $0.50 \times \mathrm{H} \rightarrow \mathrm{L}$ | 297 | 1.267 | 541.08 |
|  | $\mathrm{~S}_{3}(\mathrm{E})$ | $0.42 \times \mathrm{H} \rightarrow \mathrm{L}+3$ | 279 | 0.329 | 198.17 |
|  | $\mathrm{~S}_{1}(\mathrm{E})$ | $0.47 \times \mathrm{H}-1 \rightarrow \mathrm{~L}$ | 295 | 1.346 | 618.56 |
|  | $\mathrm{~S}_{2}(\mathrm{E})$ | $0.47 \times \mathrm{H} \rightarrow \mathrm{L}$ | 295 | 1.346 | 618.56 |
|  | $\mathrm{~S}_{3}(\mathrm{E})$ | $0.42 \times \mathrm{H}-3 \rightarrow \mathrm{~L}+0.36$ | 279 | 0.047 | 71.19 |
|  | $\mathrm{~S}_{1}(\mathrm{E})$ | $0.37 \times \mathrm{H}-1 \rightarrow \mathrm{~L}$ | 290 | 1.502 | 776.10 |
|  | $\mathrm{~S}_{2}(\mathrm{E})$ | $0.37 \times \mathrm{H} \rightarrow \mathrm{L}$ | 290 | 1.502 | 776.10 |
|  | $\mathrm{~S}_{3}(\mathrm{~A})$ | $0.42 \times \mathrm{H}-1 \rightarrow \mathrm{~L}+1+$ | 280 | 0.126 | -1213.05 |
|  | $0.42 \times \mathrm{H} \rightarrow \mathrm{L}+2$ |  |  |  |  |

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