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# **Electronic supplementary information**

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# **1** Synthetic Procedures

# 1.1 General Synthetic Methods

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H<sub>2</sub>O and <0.1 ppm O<sub>2</sub>). 1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes)<sup>1</sup>, 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolin-2-ylidene (IPr),<sup>2</sup> 1,3-bis-(2,4,6-trimethylphenyl)-4,6-diketo-5,5-dimethylpyrimidin-2-ylidene ( $^{Mes}DAC$ )<sup>3</sup>, 1,3,4,5-tetramethylimidazolin-2-ylidene (TMC)<sup>4</sup>, 1,3-di-*iso*-propyl-4,5-dimethylimidazolin-2-ylidene ( $^{i}Pr_2Im^{Me}$ )<sup>5</sup>,  $^{Ment}CAAC^6$ , Ag[Al{OC(CF<sub>3</sub>)<sub>3</sub>}<sub>4</sub>]<sup>7</sup>, AuCl(tht) (tht = tetrahydrothiophene)<sup>8</sup>, Ph<sub>2</sub>CN<sub>2</sub><sup>9</sup> and (tBuCP)<sub>2</sub> (1)<sup>10</sup> were prepared according to previously reported procedures. All other chemicals were purchased from commercial suppliers and used as received.

Solvents were dried and degassed with a MBraun SPS800solvent purification system. All dry solvents except *n*-hexane and *n*-pentane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane and *n*-pentane were stored over a potassium mirror.

# **1.2 General Analytical Techniques**

NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 300 K unless otherwise noted and internally referenced to residual solvent resonances (<sup>1</sup>H NMR: THF-d<sub>8</sub>: 1.72 ppm, C<sub>6</sub>D<sub>6</sub>: 7.16 ppm, toluene-d<sup>8</sup>: 2.08 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR: THF-d<sub>8</sub>: 25.31 ppm, C<sub>6</sub>D<sub>6</sub>: 128.06 ppm). Chemical shifts  $\delta$  are given in ppm referring to external standards of tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}), 85% phosphoric acid (<sup>31</sup>P and <sup>31</sup>P{<sup>1</sup>H} spectra). <sup>1</sup>H and <sup>13</sup>C NMR signals were assigned based on 2D NMR spectra (<sup>1</sup>H, <sup>1</sup>H-COSY, <sup>1</sup>H, <sup>13</sup>C-HSQC, <sup>1</sup>H, <sup>13</sup>C-HSQC).

UV-Vis spectra were recorded on an Ocean Optics Flame Spectrometer. Elemental analysis was performed by the central analytics department of the University of Regensburg.

## 1.3 Synthesis of Compounds

### [(TMC)PCtBu]<sub>2</sub>

To a solution of TMC (163.9 mg, 1.32 mmol, 1.0 eq) in toluene (3 mL) was added ('BuCP)<sub>2</sub> (0.58 M in toluene, 1.6 mL, 0.7 eq.). A colour change from colourless to intense orange was observed. After stirring at ambient temperature for 1 hour, a bright orange powder precipitated from the reaction mixture. Subsequently, the supernatant solution was removed by filtration and the solid was washed with toluene (0.3 mL) and dried *in vacuo*.

Crystals suitable for X-ray crystallography were grown by cooling a saturated solution of  $[(TMC)PCtBu]_2$  in THF from ambient temperature to -30 °C.



 $C_{24}H_{42}N_4P_2$ , MW = 448.58 g/mol

Yield: 204 mg (69%)

<sup>1</sup>**H NMR** (400 MHz, 300 K, THF-d<sup>8</sup>)  $\delta$  = 1.55 (s, 18H, C<sup>3</sup>H), 2.09 (s, 12H, C<sup>6</sup>H), 3.36 (s, 12H, C<sup>7</sup>H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 8.69 (s, C<sup>6</sup>), 32.1 (t, <sup>3</sup>*J*<sub>CP</sub> = 6.9 Hz, C<sup>7</sup>), 33.0 (t, <sup>3</sup>*J*<sub>CP</sub> = 6.4 Hz, C<sup>3</sup>), 43.4 (t, <sup>2</sup>*J*<sub>CP</sub> = 3.4 Hz, C<sup>2</sup>), 120.9 (t, <sup>3</sup>*J*<sub>CP</sub> = 1.7 Hz, C<sup>5</sup>), 156.6 (dd, <sup>1</sup>*J*<sub>CP</sub> = 73.5 Hz, <sup>2</sup>*J*<sub>CP</sub> 14.8 Hz, C<sup>1</sup>), 169.1 (dd, <sup>1</sup>*J*<sub>CP</sub> = 116.13 Hz, <sup>4</sup>*J*<sub>CP</sub> 7.1 Hz, C<sup>4</sup>) ppm.

<sup>31</sup>**P**{<sup>1</sup>**H**} (162 MHz, 300 K,  $C_6D_6$ )  $\delta = -28.4$  (brs) ppm.

Elemental Analysis calcd. C 64.26, H 9.44, N 12.49; found C 64.87, H 9.14, N 12.30.

UV/vis (THF):  $\lambda_{max}$  (nm,  $\varepsilon_{max}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 270 (14 000), 340 (21 000), 450 (16 000).

#### IPr=PP(CtBu)<sub>2</sub> (3a)

To a solution of IPr (200 mg, 0.52 mmol, 1.0 eq) in toluene (10 mL) was added ('BuCP)<sub>2</sub> (3.6 mL, 0.58 mol/L, 2.08 mmol, 4.0 equiv.). After stirring at ambient temperature for three weeks, the reaction was completed according to <sup>1</sup>H NMR monitoring. The solvent was removed and the light yellow residue was dried *in vacuo*. Recrystallisation of the residue from *n*-pentane

at -30 °C overnight affords a mixture of **3a** and (*t*BuCP)<sub>4</sub> (ca. 1:1). Subsequently, (*t*BuCP)<sub>4</sub> was removed by sublimation at 120 °C on a turbomolecular pump (p < 1.10<sup>-4</sup> mbar) for three days. The resulting yellow powder was pure according to NMR and elemental analysis. Single crystals suitable for X-ray crystallography were grown by cooling a saturated solution of **3a** from ambient temperature to -30 °C.



 $C_{37}H_{54}N_2P_2$ , MW = 588.80 g/mol

Yield: 91 mg (29%)

<sup>1</sup>**H** NMR (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta = 1.20$  (d, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 12H, C<sup>11</sup>H), 1.23 (s, 18H, C<sup>3</sup>H), 1.62 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, C<sup>11</sup>H), 3.20 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz, 4H, C<sup>10</sup>H), 6.14 (s, 2H, C<sup>5</sup>H), 7.14 (d, <sup>3</sup>*J*<sub>HH</sub> = 2.0 Hz, 4H, C<sup>8</sup>H), 6.61 (dd, <sup>3</sup>*J*<sub>HH</sub> = 6.2/8.9 Hz, 2H, C<sup>9</sup>H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta = 23.7$  (s, C<sup>11</sup>), 24.7 (s, C<sup>12</sup>), 29.1 (s, C<sup>10</sup>), 30.9 (d, <sup>3</sup>*J*<sub>CP</sub> = 1.8 Hz, C<sup>3</sup>), 33.3 (dd, <sup>2</sup>*J*<sub>CP</sub> = 6.5 Hz, <sup>3</sup>*J*<sub>CP</sub> = 1.2 Hz, C<sup>2</sup>), 119.8 (d, <sup>3</sup>*J*<sub>CP</sub> = 3.7 Hz, C<sup>5</sup>), 124.1 (dd, <sup>1</sup>*J*<sub>CP</sub> = 50.1 Hz, <sup>2</sup>*J*<sub>CP</sub> = 8.6 Hz, C<sup>1</sup>), 124.6 (s, C<sup>9</sup>), 130.3 (s, C<sup>8</sup>), 135.8 (d, <sup>3</sup>*J*<sub>CP</sub> = 3.4 Hz, C<sup>6</sup>), 147.4 (s, C<sup>7</sup>), 176.7 (dd, <sup>1</sup>*J*<sub>CP</sub> = 115.9 Hz, <sup>2</sup>*J*<sub>CP</sub> = 4.0 Hz, C<sup>4</sup>) ppm.

<sup>31</sup>**P**{<sup>1</sup>**H**} (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta = -172.3$  (d, <sup>1</sup>*J*<sub>PP</sub> = 296 Hz), -39.4 (d, <sup>1</sup>*J*<sub>PP</sub> = 296 Hz) ppm.

Elemental Analysis calcd. C 75.48, H 9.24, N 4.76; found C 75.41, H 8.98, N 4.44.

UV/vis (THF):  $\lambda_{\text{max}}$  (nm,  $\varepsilon_{\text{max}}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 300 (10 500), 360 (15 000).

#### IMes=PP(CtBu)<sub>2</sub> (3b)

To a solution of IMes (150 mg, 0.5 mmol, 1.0 eq) in toluene (10 mL) was added  $(tBuCP)_2$  (0.59 M in toluene, 3.5 mL, 2.1 mmol, 4.0 eq.). After stirring at ambient temperature for two weeks, the reaction was completed according to <sup>1</sup>H NMR monitoring. The solvent was removed and the light yellow residue was dried *in vacuo*. Subsequently,  $(tBuCP)_4$  was removed by

sublimation at 120 °C on a turbomolecular pump (p <  $1 \cdot 10^{-4}$  mbar) for three days. The resulting yellow powder was pure according to NMR and elemental analysis. Single crystals suitable for X-ray crystallography were grown by cooling a saturated solution of **3b** from ambient temperature to -30 °C.



 $C_{31}H_{42}N_2P_2$ , MW = 504.64 g/mol

Yield: 73 mg (30%)

<sup>1</sup>**H** NMR (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 1.23 (s, 18H, C<sup>3</sup>H), 2.08 (s, 6H, C<sup>11</sup>H), 2.32 (s, 12H, C<sup>10</sup>H), 5.88 (s, 2H, C<sup>5</sup>H), 6.78 (s, 4H, C<sup>8</sup>H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 18.7 (s, C<sup>10</sup>), 21.1 (s, C<sup>11</sup>), 30.8 (d <sup>4</sup>*J*<sub>CP</sub> = 1.8 Hz C<sup>3</sup>), 33.0 (dd, <sup>2</sup>*J*<sub>CP</sub> = 6.6 Hz, <sup>3</sup>*J*<sub>CP</sub> = 1.1 Hz, C<sup>2</sup>), 118.6 (d, <sup>3</sup>*J*<sub>CP</sub> = 3.6 Hz, C<sup>5</sup>), 125.6 (dd, <sup>1</sup>*J*<sub>CP</sub> = 50.4 Hz, <sup>2</sup>*J*<sub>CP</sub> = 9.0 Hz, C<sup>1</sup>), 129.7 (s, C<sup>8</sup>), 135.5 (d, <sup>3</sup>*J*<sub>CP</sub> = 2.6 Hz, C<sup>6</sup>), 136.7 (s, C<sup>7</sup>), 138.7 (s, C<sup>9</sup>), 172.9 (dd, <sup>1</sup>*J*<sub>CP</sub> = 113.9 Hz, <sup>2</sup>*J*<sub>CP</sub> = 7.0 Hz, C<sup>4</sup>) ppm.

<sup>31</sup>**P**{<sup>1</sup>**H**} (162 MHz, 300 K,  $C_6D_6$ )  $\delta = -169.9$  (d,  ${}^{1}J_{PP} = 299$  Hz), -47.2 (d,  ${}^{1}J_{PP} = 299$  Hz) ppm.

Elemental Analysis calcd C 73.78, H 8.39, N 5.08; found C 74.05, H 8.67, N 5.43.

UV/vis (THF):  $\lambda_{\text{max}}$  (nm,  $\varepsilon_{\text{max}}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 300 (15 000), 360 (15 500).

Compounds **3a** and **3b** are very sensitive towards hydrolysis, forming the known NHC=PH (NHC = IPr, IMes) compounds.<sup>11–14</sup>

#### MesDAC=PP(CtBu)<sub>2</sub> (3c)

To a solution of <sup>Mes</sup>DAC (150 mg, 0.4 mmol, 1.0 eq) in toluene (10 mL) was added (*t*BuCP)<sub>2</sub> (0.26 M in toluene, 1.5 mL, 0.65 mmol, 1.6 eq.). After stirring at ambient temperature for two weeks, the reaction was completed according to <sup>1</sup>H NMR monitoring. The solvent was removed and the light yellow residue was dried *in vacuo*. Subsequently, the residue was dissolved in benzene (5 mL) and layered with *n*-hexane (25 mL). Storage at -30 °C overnight afforded yellow crystals which were isolated by decanting the supernatant and dried under reduced

pressure. <sup>1</sup>H NMR analysis of the material shows the presence of 0.5 equivalents of *n*-hexane (see Figure S14). This material was used for elemental analysis and UV/Vis spectroscopy. Further drying of the material under reduced pressure affords *n*-hexane-free **3c** which was used for NMR analysis.

Single crystals suitable for X-ray crystallography were grown by slow diffusion of n-hexane into a saturated solution of 3c in benzene at ambient temperature.



 $C_{34}H_{46}N_2O_2P_2$ , MW = 576.70 g/mol

Yield: 130 mg (56%)

<sup>1</sup>**H NMR** (400 MHz, 300 K,  $C_6D_6$ )  $\delta = 0.99$  (s, 18H,  $C^3H$ ), 1.73 (s, 6H,  $C^7H$ ), 1.99 (s, 3H  $C^{13}H$ ), 2.07 (s, 3H,  $C^{19}H$ ), 2.24 (s, 6H,  $C^{18}H$ ), 2.39 (s, 6H,  $C^{12}H$ ), 6.71 (s, 2H,  $C^{10}H$ ), 6.89 (s, 2H,  $C^{16}H$ ) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 18.0 (d, <sup>5</sup>*J*<sub>CP</sub> = 3.0 Hz, C<sup>18</sup>), 18.4 (d, <sup>5</sup>*J*<sub>CP</sub> = 1.9 Hz, C<sup>12</sup>), 21.1 (s, C<sup>13</sup>), 21.2 (s, C<sup>19</sup>), 24.4 (s, C<sup>7</sup>), 29.7 (d, <sup>4</sup>*J*<sub>CP</sub> = 1.5 Hz, C<sup>3</sup>), 32.5 (dd, <sup>2</sup>*J*<sub>CP</sub> = 6.5 Hz, <sup>3</sup>*J*<sub>CP</sub> = 2.0 Hz, C<sup>2</sup>), 48.0 (s, C<sup>6</sup>), 125.6 (dd, <sup>1</sup>*J*<sub>CP</sub> = 51.8 Hz, <sup>2</sup>*J*<sub>CP</sub> = 8.7 Hz, C<sup>1</sup>), 129.8 (s, C<sup>10</sup>), 131.0 (d, <sup>5</sup>*J*<sub>CP</sub> = 2.7 Hz, C<sup>16</sup>), 135.0 (d, <sup>3</sup>*J*<sub>CP</sub> = 4.8 Hz, C<sup>8</sup>), 135.9 (d, <sup>4</sup>*J*<sub>CP</sub> = 4.4 Hz, C<sup>9</sup>), 137.0 (d, <sup>3</sup>*J*<sub>CP</sub> = 9.0 Hz, C<sup>14</sup>), 137.5 (d, <sup>4</sup>*J*<sub>CP</sub> = 8.4 Hz, C<sup>15</sup>), 138.4 (s, C<sup>11</sup>), 139.0 (s, C<sup>17</sup>), 167.9 (d, <sup>3</sup>*J*<sub>CP</sub> = 2.6 Hz, C<sup>5</sup>), 168.4 (s, C<sup>5°</sup>), 173.7 (dd, <sup>1</sup>*J*<sub>CP</sub> = 92.5 Hz, <sup>2</sup>*J*<sub>CP</sub> = 2.0 Hz, C<sup>4</sup>) ppm.

<sup>31</sup>P{<sup>1</sup>H} (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta = -162.9.8$  (d, <sup>1</sup>*J*<sub>PP</sub> = 312 Hz), 139.0 (d, <sup>1</sup>*J*<sub>PP</sub> = 312 Hz) ppm.

**Elemental Analysis** was performed with a sample recrystallised from *n*-hexane (containing 0.5 eq. *n*-hexane, see Figure S14) calcd. C 71.70, H 8.62, N 4.52; found C 71.89, H 8.31, N 4.89.

UV/vis (THF):  $\lambda_{\text{max}}$  (nm,  $\varepsilon_{\text{max}}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 260 (13 000sh), 360 (21 500).

#### (TMC)C(S)(NPh)

Phenyl isothiocyanate (0.1 mL, 113 mg, 0.84 mmol, 2.1 equiv.) was added to a solution of TMC (50.0 mg, 0.4 mmol, 1.0 equiv.) in 0.5 mL C<sub>6</sub>D<sub>6</sub>. The reaction mixture turned yellow immediately and was stirred for 18 h. Subsequently, the solvent was removed *in vacuo*. Crystallisation from toluene/*n*-hexane (1/1, 2 mL/2 mL) afforded yellow crystals of [(TMC)=C(S)(NPh)] suitable for single crystal X-ray diffraction experiments, which were isolated by decanting the supernatant and dried *in vacuo*.



 $C_{14}H_{16}N_3S$ , MW = 259.37 g/mol

**Yield:** 32 mg (31%)

<sup>1</sup>**H** NMR (400 MHz, 300 K,  $C_6D_6$ )  $\delta = 1.00$  (s, 6H,  $C^5H$ ), 3.07 (s, 6H,  $C^4H$ ), 7.10-7.15 (m, 1H, C<sup>9</sup>H, overlapping with  $C_6D_6$  signal), 7.47-7.55 (m, 2H,  $C^8H$ ), 8.39-8.45 (m, 2H,  $C^7H$ ) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 7.27 (s, C<sup>5</sup>), 31.4 (s, C<sup>4</sup>), 121.7 (s, C<sup>3</sup>), 123.7 (s, C<sup>9</sup>), 124.3 (s, C<sup>7</sup>), 128.6 (s, C<sup>8</sup>), 147.0 (s, C<sup>1</sup>), 152.4 (s, C<sup>2</sup>), 167.8 (s, C<sup>6</sup>) ppm.

Elemental Analysis calcd. C 64.83, H 6.41, N 16.20; found C 65.01, H 6.47, N 16.09.

UV/vis (THF):  $\lambda_{\text{max}}$  (nm,  $\varepsilon_{\text{max}}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 260 (12 000sh), 340 (12 000).

### (TMC)=N-N=CPh<sub>2</sub>

1,1'-(Diazomethylene)bis[benzene] (78 mg, 0.4  $\mu$ mol, 1.0 equiv.) in C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added to a solution of TMC (50.0 mg, 0.4 mmol, 1.0 equiv.) in C<sub>6</sub>D<sub>6</sub> (0.5 mL). The orange reaction mixture was stirred for 18 h. Subsequently, the solvent was removed *in vacuo*. Crystallisation from toluene/*n*-hexane (1/1, 2 mL/2 mL) afforded bright orange crystals of [(TMC)-N=N-CPh<sub>2</sub>] suitable for single crystal X-Ray diffraction experiments, which were isolated by decanting the supernatant and dried *in vacuo*.



 $C_{20}H_{22}N_4$ , MW = 318.42 g/mol

Yield: 80 mg (63%)

<sup>1</sup>**H NMR** (400 MHz, 300 K,  $C_6D_6$ )  $\delta = 1.31$  (s, 6H,  $C^5H$ ), 3.14 (s, 6H,  $C^4H$ ), 7.11-7.18 (m, 1H, C<sup>9</sup>H), 7.19-7.25 (m, 1H, C<sup>13</sup>H), 7.25-7.31 (m, 2H, C<sup>8</sup>H), 7.33-7.41 (m, 2H, C<sup>12</sup>H), 7.73-7.81 (m, 2H, C<sup>11</sup>H), 7.91-7.98 (m, 2H, C<sup>7</sup>H) ppm.

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 300 K,  $C_6D_6$ )  $\delta = 8.1$  (s,  $C^5$ ), 30.6 (s,  $C^4$ ), 115.8 (s,  $C^3$ ), 126.5 (s,  $C^9$ ), 126.9 (s,  $C^{13}$ ), 127.2 (s,  $C^7$ ), 127.9 (s,  $C^{12}$ , overlapping with  $C_6D_6$ -signal), 128.3 (s,  $C^8$ , overlapping with  $C_6D_6$ -signal), 131.2 (s,  $C^{11}$ ), 138.9 (s,  $C^{10}$ ), 142.4 (s,  $C^6$ ), 148.3 (s,  $C^2$ ), 151.6 (s,  $C^1$ ) ppm.

UV/vis (THF):  $\lambda_{\text{max}}$  (nm,  $\varepsilon_{\text{max}}$  /L·mol<sup>-1</sup>·cm<sup>-1</sup>) 240 (16 000), 320 (8900), 400 (30 000).

Elemental Analysis calcd. C 75.44, H 6.96, N 17.60; found C 76.00, H 6.62, N 17.62.

## **1.4 Additional Experiments**



Figure S 1. Reactivity of 2 toward transition metal complexes and heterocumulenes.

### Reaction of 2 with [AuCl(tht)]

[AuCl(tht)] (11 mg, 33  $\mu$ mol, 1.0 eq.) was dissolved in THF (1.0 mL) and added to a yellow solution of **2** (15 mg, 33  $\mu$ mol, 1.0 eq.) in THF (1.5 mL) at – 30 °C. The orange solution turned cloudy whilst stirring overnight and was analysed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure S 22). Subsequently, the solvent was removed *in vacuo* and the residue was recrystallised from dichloromethane. Colourless crystals formed upon storage at –30 °C overnight were identified as [(TMC)<sub>2</sub>Au]Cl(DCM) by single crystal X-ray crystallography.<sup>15</sup>

## Reaction of 2 with Ag[Al{OC(CF<sub>3</sub>)<sub>3</sub>}<sub>4</sub>]

A colourless solution of Ag[Al{OC(CF<sub>3</sub>)<sub>3</sub>}<sub>4</sub>] (28 mg, 22  $\mu$ mol, 0.5 equiv.) in dichloromethane (1.5 mL) was added to **2** (20 mg, 45  $\mu$ mol, 1.0 equiv.) in tetrahydrofurane (3 mL) at -30 °C The solution turned intense orange while stirring overnight and was analysed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure S 23).

## Reaction of 2 with [(p-cymene)RuCl<sub>2</sub>]<sub>2</sub>

An orange solution of [p-cymeneRuCl<sub>2</sub>]<sub>2</sub> (14 mg, 22 µmol, 0.5 equiv.) in THF (7 mL) was added to **2** (20 mg, 45 µmol, 1.0 equiv.) in THF (3 mL). The reaction mixture turned red whilst stirring overnight and was analysed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure S 24).

## Reaction of 2 with [(cod)RhCl]<sub>2</sub>

A solution of  $[(cod)RuCl]_2$  (13 mg, 27 µmol, 0.8 equiv.) in THF (1 mL) was added to an orange solution of **2** (15.0 mg, 33.4 µmol, 1.0 equiv.) in THF (1 mL) at -30 °C. The reaction mixture was stirred overnight whilst turning brown and was analysed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Figure S 25).

## Reaction of 1 with MentCAAC

To a solution of <sup>Ment</sup>CAAC (50 mg, 0.13 mmol, 1.0 eq) in toluene (10 mL) was added ( ${}^{t}BuCP$ )<sub>2</sub> (0.59 M in toluene, 0.5 mL, 0.3 mmol, 2.3 eq.). After stirring at ambient temperature in the dark for two weeks, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed the presence of starting material (1 + <sup>Ment</sup>CAAC) and (tBuCP)<sub>4</sub> (see Figure S 26). Stirring at ambient temperature for another two weeks did not result in any further change of the integral ratios.

## Reaction of 1 with and *i*Pr<sub>2</sub>Im<sup>Me</sup>

To a solution of  $iPr_2Im^{Me}$  (30 mg, 0.17 mmol, 1.0 eq) in toluene (10 mL) was added ( $^tBuCP$ )<sub>2</sub> (0.59 M in toluene, 0.5 mL, 0.3 mmol, 2.4 eq.). After stirring at ambient temperature in the dark

for two weeks, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed the presence of starting material  $(1 + iPr_2Im^{Me})$  and  $(tBuCP)_4$  and two other, unidentified species (see <sup>31</sup>P{<sup>1</sup>H} NMR spectrum in Figure S 27). Stirring at ambient temperature for another two weeks did not result in any further change of the integral ratios.

# 2 NMR Spectra



Figure S3. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100 MHz, 300 K, THF-d<sub>8</sub>) of 2; \*THF-d<sub>8</sub>.



Figure S4. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, THF-d<sub>8</sub>) of 2; \*minor amount of 1 (*t*BuCP)<sub>2</sub>.



Figure S5. Variable Temperature <sup>1</sup>H NMR spectra (400 MHz, THF-d<sub>8</sub>) of 2; \*THF-d<sub>8</sub>.





**Figure S7.** <sup>1</sup>H NMR spectrum (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of **3a**; \*C<sub>6</sub>D<sub>6</sub>.



Figure S8.  ${}^{13}C{}^{1}H$  NMR spectrum (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of 3a; \*C<sub>6</sub>D<sub>6</sub>.



Figure S9. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of **3a**; \*minor unknown impurity (<2%).



Figure S11. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of **3b**; \*C<sub>6</sub>D<sub>6</sub>.



Figure S12. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of **3b**; \*minor amount of **1** (*t*BuCP)<sub>4</sub> (<3%).



Figure S13. <sup>1</sup>H NMR spectrum (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of 3c; \*C<sub>6</sub>D<sub>6</sub>.



Figure S15. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of 3c; \*C<sub>6</sub>D<sub>6</sub>.



Figure S16. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of 3c; \*minor amount of (*t*BuCP)<sub>4</sub> (<1%).



 $\label{eq:Figure S17. } \textbf{Figure S17. } ^{31}P\{^{1}H\} \text{ NMR spectra (162 MHz, 300K, $C_6D_6$) of $\textbf{3a}$ (top), $\textbf{3b}$ (middle) and $\textbf{3c}$ (bottom).}$ 



Figure S 18. <sup>1</sup>H NMR spectrum (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of [(TMC)=C(S)(NPh)]; \*C<sub>6</sub>D<sub>6</sub>.



Figure S 19.  ${}^{13}C{}^{1}H$  NMR spectrum (100 MHz, 300 K,  $C_6D_6$ ) of [(TMC)=C(S)(NPh)];  $*C_6D_6$ .



Figure S 20: <sup>1</sup>H NMR spectrum (400 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of [(TMC)-N=N-CPh<sub>2</sub>]; \*C<sub>6</sub>D<sub>6</sub>.



Figure S 21. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (100 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of [(TMC)-N=N-CPh<sub>2</sub>]; \*C<sub>6</sub>D<sub>6</sub>.



Figure S 22. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 2 with AuCl(tht).  $(tBuCP)_4$ ,  $(tBuCP)_2$ 



Figure S 23. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 2 with Ag[Al{OC(CF<sub>3</sub>)<sub>3</sub>}];  $(tBuCP)_{4,}$  $(tBuCP)_{2.}$ 



Figure S 24. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 2 with [(*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub>;  $\blacklozenge$  (*t*BuCP)<sub>4</sub>.



Figure S 25. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 2 with [(cod)RuCl]<sub>2</sub>;  $\blacklozenge$  (*t*BuCP)<sub>4</sub>.



Figure S 26. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 1 with <sup>Ment</sup>CAAC; ° (*t*BuCP)<sub>4</sub>.



Figure S 27. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>) of the reaction of 1 with *i*Pr<sub>2</sub>Im<sup>Me</sup>; ° (*t*BuCP)<sub>4</sub>.

# 3 UV-Vis Spectra



Figure S28. UV/vis spectrum of 2 recorded in THF.



Figure S29. UV/vis spectrum of 3a recorded in THF.



Figure S30. UV/vis spectrum of 3b recorded in THF.



Figure S31. UV/vis spectrum of 3c recorded in THF.



Figure S 32. UV/vis spectrum of [(TMC)=C(S)(NPh)] recorded in THF.



Figure S 33. UV/vis spectrum of [(TMC)-N=N-CPh<sub>2</sub>] recorded in THF.

## **4** Single Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku Oxford Diffraction SuperNova Atlas diffractometers with Cu- $K_{\alpha}$  radiation ( $\lambda$ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N<sub>2</sub> cooling device. Either semi-empirical multi-scan absorption corrections<sup>16,17</sup> or analytical ones<sup>18</sup> were applied to the data. The structures were solved with SHELXT<sup>19</sup> solution program using dual methods and by using Olex2 as the graphical interface.<sup>20</sup> The models were refined with ShelXL<sup>21</sup> using full matrix least squares minimization on F<sup>2</sup>.<sup>22</sup> The hydrogen atoms were located in idealized positions and refined isotropically with a rigid model. The disorder in **3a**, **3c** and (TMC)=N-N=CPh<sub>2</sub> were treated with soft displacement parameters and geometrical restraints.

Despite numerous crystallisation attempts, only poor quality crystals could be obtained of compound 3c. Numerous samples were tested for diffraction, but most crystals turned out to be twinned or only weakly diffracting, especially at higher resolution. Moreover, positional disorder over two positions in the phosphirene moiety was found. The presented dataset was tailored to the best compromise between completeness, frame exposure and total dose time.



**Figure S 34.** Molecular structure of **3b** in the solid state. H atoms and the second, crystallographically independent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.2225(8), P2–C1 1.835(2), P2–C2 1.841(2), P1–C11 1.768(2), C1–C2 1.297(3), C1-P2-C2 41.31(10), C1-P2-P1 99.19(7), C2-P2-P1 99.40(7), C2-C1-P2 69.59(14), C1-C2-P2 69.10(13), C11-P1-P2 105.30(7).



**Figure S 35.** Molecular structure of (TMC)C(S)(NPh) in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and the second, crystallographically independent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: S1–C1 1.7118(15), N1–C1 1.2923(19), C1–C2 1.4918(19), N2–C2 1.3378(19), N3–C2 1.3409(19), N1-C1-S1 131.91(11), N1-C1-C2 113.33(13), C2-C1-S1 114.68(10), N2-C2-N3 107.41(12).



Figure S 36. Molecular structure of (TMC)=N-N=CPh<sub>2</sub> in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and a minor disordered component of N1/N2 are omitted for clarity. Selected bond lengths [Å] and angles [°]:N2A-N1A 1.361(2), N2A-C1 1.315(2), N1A-C2 1.340(2), N3-C2 1.345(2), N4-C2 1.375(2), C1-N2A-N1A 113.09(16), C2-N1A-N2A 115.28(16), N3-C2-N4 106.21(15).

Table S

Compound	2	3a	3b	3c	(TMC)C(S)(NPh)	(TMC)=N-N=CPh <sub>2</sub> )
CCDC	2040302	2040304	2040303	2040305	2040306	2040301
Empirical formula	$C_{24}H_{42}N_4P_2$	$C_{37}H_{54}N_2P_2$	$C_{31}H_{42}N_2P_2$	$C_{34}H_{46}N_2O_2P_2$	$C_{14}H_{17}N_3S$	$C_{20}H_{23}N_4$
Formula weight	448.55	588.76	504.60	574.48	259.36	319.42
Temperature/K	290(13)	123.01(10)	123.01(10)	123.00(10)	123.00(10)	151(40)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/n$	P-1	P-1
a/Å	15.7329(4)	11.8598(2)	8.5803(2)	18.4310(12)	7.5819(2)	8.0986(3)
b/Å	8.3859(2)	18.0388(3)	10.6253(2)	8.6721(7)	12.0396(4)	9.9827(4)
c/Å	19.9061(4)	17.3344(2)	35.5315(8)	20.5999(13)	15.5332(6)	11.1882(4)
α/°	90	90	93.857(2)	90	87.680(3)	87.935(3)
β/°	94.152(2)	92.7130(10)	95.926(2)	94.086(6)	88.235(3)	77.417(4)
γ/°	90	90	110.711(2)	90	72.214(3)	73.219(3)
Volume/Å <sup>3</sup>	2619.41(11)	3704.30(10)	2995.00(12)	3284.2(4)	1348.79(8)	844.85(6)
Z	4	4	4	4	4	2
$\rho_{calc}g/cm^3$	1.137	1.056	1.119	1.162	1.277	1.256
µ/mm⁻¹	1.624	1.238	1.458	1.436	2.004	0.593
F(000)	976.0	1280.0	1088.0	1235.0	552.0	342.0
Crystal size/mm <sup>3</sup>	$0.207 \times 0.112 \times 0.033$	$0.702 \times 0.372 \times 0.279$	$0.143 \times 0.119 \times 0.044$	$0.345 \times 0.298 \times 0.052$	$0.413 \times 0.244 \times 0.084$	$0.567 \times 0.404 \times 0.145$
Radiation	$CuK\alpha (\lambda = 1.54184)$	$CuK\alpha (\lambda = 1.54184)$	$CuK\alpha (\lambda = 1.54184)$	$CuK\alpha \ (\lambda = 1.54184)$	$CuK\alpha (\lambda = 1.54184)$	$CuK\alpha (\lambda = 1.54184)$
2\Overlap range for data collection/°	8.908 to 148.138	7.076 to 146.798	7.552 to 147.074	8.606 to 134.134	7.716 to 145.492	9.256 to 145.362
	$-19 \le h \le 18$ ,	$-14 \le h \le 14$ ,	$-10 \le h \le 10$ ,	$-22 \le h \le 20$ ,	$-9 \le h \le 7,$	$-9 \le h \le 9,$
Index ranges	$-10 \le k \le 10$ ,	$-21 \le k \le 22$ ,	$-10 \le k \le 13$ ,	$-9 \le k \le 10$ ,	$-14 \le k \le 13$ ,	$-12 \le k \le 8, -$
	$-24 \le 1 \le 22$	$-20 \le 1 \le 21$	$-44 \le 1 \le 43$	$-17 \le 1 \le 24$	<b>-</b> 19 ≤ 1 ≤ 18	$13 \le l \le 13$
Reflections collected	11361	16465	20271	9705	9306	5328
Indonandant raflactions	$5186 [R_{int} = 0.0246,$	$7280 [R_{int} = 0.0179]$	$11591 [R_{int} = 0.0299,$	$5526 [R_{int} = 0.0783,$	$5154 [R_{int} = 0.0241,$	$3156 [R_{int} = 0.0189,$
independent reflections	$R_{sigma} = 0.0273$ ]	$R_{sigma} = 0.0205$ ]	$R_{sigma} = 0.0484$ ]	$R_{sigma} = 0.1153$ ]	$R_{sigma} = 0.0314$ ]	$R_{sigma} = 0.0220$ ]
Data/restraints/para- meters	5186/0/285	7280/39/414	11591/0/655	5526/169/482	5154/0/333	3156/36/240
Goodness-of-fit on F <sup>2</sup>	1.024	1.045	1.026	1.042	1.037	1.044
Final R indexes [I>=2 $\sigma$	$R_1 = 0.0403$ ,	$R_1 = 0.0363$ ,	$R_1 = 0.0500$ ,	$R_1 = 0.0830$ ,	$R_1 = 0.0364$ ,	$R_1 = 0.0556$ ,
[(I)]	$wR_2 = 0.1067$	$wR_2 = 0.0964$	$wR_2 = 0.1221$	$wR_2 = 0.1821$	$wR_2 = 0.0961$	$wR_2 = 0.1558$
Final R indexes [all	$R_1 = 0.0505$ ,	$R_1 = 0.0390,$	$R_1 = 0.0647$ ,	$R_1 = 0.1502$ ,	$R_1 = 0.0404,$	$R_1 = 0.0592,$
data]	$wR_2 = 0.1143$	$wR_2 = 0.0987$	$wR_2 = 0.1317$	$wR_2 = 0.2086$	$wR_2 = 0.1003$	$wR_2 = 0.1597$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.23	0.27/-0.29	0.37/-0.33	0.30/-0.37	0.28/-0.30	0.54/-0.31

# 5 Quantum Chemical Calculations

### **General Methods**

All calculations were performed with the ORCA program package.<sup>23</sup> All calculations were conducted in the gas phase. The RI<sup>24</sup> approximation was used for GGA calculations whereas the RIJCOSX<sup>25</sup> approximation was used for hybrid-DFT calculations. Geometry optimisations have been carried out at the BP86-D3BJ/def2-TZVP<sup>26–30</sup> level of theory. Thereby, the aryl substituents at the NHC moieties were truncated to phenyl rings (NHC = IPh (1,3-diphenylimidazolin-2-ylidene)). Intrinsic bond orbitals (IBOs) have been constructed from the occupied BP86 orbitals according to Knizia *et al.*<sup>31</sup> TD-DFT calculations were performed on the wB97X-D3/def2-SVP<sup>32</sup> level of theory and GaussSum<sup>33</sup> was used to visualise the results.

#### **Density difference plots**



Figure S 37: Density difference plot (isosurface value 0.01) for the transition at 450 nm caused mainly by a HOMO-LUMO transition ( $n_P \rightarrow \pi^*_{CC}$ ) for 2. The transition occurs from blue  $\rightarrow$  red.



Figure S 38: Calculated UV/VIS Spectrum for 2 as visualised by GaussSum.



Figure S 39: Density difference plot (isosurface value 0.01) for the transition at 360 nm caused mainly by a HOMO-LUMO transition for (IPh)PP(CtBu)<sub>2</sub>. The transition occurs from blue  $\rightarrow$  red.



Figure S 40: Calculated UV/VIS Spectrum for (IPh)PP(CtBu)<sub>2</sub> as visualised by GaussSum.

## **Cartesian Coordinates for Optimised Structures**

2:

Р	4.52516715511791	2.48065643079355	3.39236715085063
Р	2.91112346262265	2.62083834140304	7.52923813787542
Ν	5.00888339384399	5.22270354511455	2.52178032859559
Ν	5.63187548011858	3.63212636781320	1.15938588114814
Ν	1.89969992450498	5.31489348951829	8.00661830306115
Ν	1.57552256307653	3.84577781192967	9.59122599573389
С	5.07405440980034	3.84189293596235	2.41251979108958
С	5.50763353561199	5.83791766478722	1.36352757011603
С	2.09841122065270	3.97713806175743	8.31261557640173
С	4.28806635567537	3.12583935810668	5.12272061817684
С	3.04431297377538	3.04741342463565	5.72207517710754
С	5.88501828960876	4.84311313550106	0.50876747113664
С	5.63004025099947	3.34563315341792	5.91671021099667
С	1.27877146480482	5.98266867966557	9.07310693596211
С	1.08829614544149	5.06661642912846	10.06669110943350
С	1.69618586230946	2.88903335212317	4.92397302962304
С	5.86210516496124	2.30588059738929	0.63281114549536
Н	6.32945902695700	1.68889836174668	1.41672976143283
Н	6.51860542634570	2.36535815963926	-0.24180732355543
Η	4.91374063730109	1.82101228363322	0.35007447747707
С	5.56717009521720	7.31674222707925	1.22172188643552

Η	4.57036128830776	7.78073961098635	1.29324265465154
Η	5.98843318053989	7.58494419905281	0.24539085771354
Η	6.19931476290186	7.77960621061721	1.99654940758512
С	6.03674571896595	2.01131313984368	6.58035735450738
Η	5.29721923440082	1.69247180882098	7.32600864255358
Η	7.01179653341212	2.11996161471612	7.08278273808805
Η	6.12721915171246	1.22767367771056	5.81358671032045
С	1.60012013708163	2.59024437646264	10.30696773419743

# (IPh)PP(CtBu)<sub>2</sub>:

-			
P	2.87186623820695	4.87741704658394	11.90864259877218
P	3.97079430196542	6.80468619211665	11.5253169438/042
Ν	2.70256314664553	9.30966612384833	11.84185948426615
Ν	1.94317170920530	7.83568264021944	13.28644248679334
С	2.62162742108278	10.75774417718113	9.88893676124389
С	3.35518023052869	9.93028322768038	10.75109445921696
С	2.87541231507736	7.97764070307693	12.25709840272294
С	4.71991442204510	9.71286058680685	10.52404842762294
С	1.87705617452494	6.76066361674719	14.21966569521741
С	0.63896512998081	6.18597659087902	14.51672832368624
С	4.25735431543161	3.69205699894395	11.65014030830400
С	3.59858828280957	3.88328622467979	10.52949424696750
С	1.67524810354612	9.91618235920368	12.56661354373359
Η	1.41641646817981	10.95624251391938	12.41994315863684
С	3.25611145159723	11.37111178825715	8.80975311357452
Н	2.67843134969555	12.00808597935160	8.13893485711227
С	5.34118599511710	10.32281978765113	9.43325769620516
Н	6.40394679286489	10.14955301488048	9.26032173016405
С	1.20160133833675	9.00703364493121	13.44882475071079
Н	0.45507540181053	9.09639055415736	14.22705517005674
С	3.03887842028685	6.32844503111504	14.86665578170123
С	4.61734940890980	11.15308101568269	8.57506070583166
Η	5.10905852091531	11.62593529345006	7.72439698792020
С	2.95669578433825	5.29533665769881	15.79707495533607
Н	3.86196384871094	4.95144184666615	16.29789291306349
С	0.56589681631561	5.15834984954988	15.45827972637895
Н	-0.39795110752395	4.69925667124310	15.68052156137903
С	5.46510209466534	3.10705807796427	12.31951020026804
С	1.72350884467169	4,70428850464797	16.09304657138793
Н	1.66701566709926	3.89125798801846	16.81748869781741
С	3.48985156263782	3.65224578794483	9.05769079267893
Ċ	2.00651890315075	3,45912924485665	8.69131345467375
Н	1 58967075174268	2 57387501430049	9 19270182165805
Н	1 89414158442403	3 32862744287471	7 60468573179754
Н	1 41864117445629	4 33390451805653	9 00202433192563
С	4 30125801194928	2 41036237756488	8 65001485146952
н	5 36395259318671	2 53594575446298	8 90104181685716
Н	4 22551763449434	2 24491294248258	7 56468548022276
Н	3 92906126299269	1 51136237032945	9 16138053408416
	2./2/001202//20/	1.0110000010000770	2.10120022100110

С	4.03820376270199	4.90103410413775	8.33324762072342
Η	3.49696294956997	5.80382297764392	8.64616577883255
Η	3.93136242980816	4.77747253249528	7.24430571879657
Η	5.10057095584639	5.05412656526030	8.56792423540883
С	6.72221588214685	3.72801311767304	11.67385044129591
С	5.43142641614828	3.45431542151179	13.81623756853068
С	5.47236627067199	1.57796884677979	12.13202377335237
Η	5.42865016496124	4.54485099179936	13.95070547199805
Η	6.30938918319680	3.03677860454278	14.33122674119087
Η	4.52244138416219	3.05587072158711	14.28757336717011
Η	5.50623915986180	1.31148942906826	11.06750482533628
Η	4.57084597606333	1.12675300887442	12.56994184053215
Η	6.35317785259191	1.13975372900901	12.62574583638078
Η	6.77695518278076	3.47918889591537	10.60497149989481
Η	7.63096643347916	3.34797201638978	12.16628045152224
Η	6.70235848207707	4.82262559277510	11.76878354923495
Η	1.55157128506228	10.89273231835745	10.04788959179648
Η	5.28641764485399	9.08225308560299	11.20721314642112
Η	3.99326659433725	6.78582924083338	14.60885642702599
Η	-0.25155037639713	6.52117863971796	13.98438303922634

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