Electronic Supplementary Information (ESI) for

Stereoselective photoreaction in P-stereogenic dithiazoylbenzo[b]phosphole chalcogenides

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1. NMR characterizations

**Fig. S1** $^1$H NMR spectrum of rac-1a in CDCl$_3$.

**Fig. S2** $^{13}$C NMR spectrum of rac-1a in CDCl$_3$. 

S2
Fig. S3 $^{31}$P NMR spectrum of rac-1a in CDCl$_3$.

Fig. S4 $^1$H NMR spectrum of rac-2a in CDCl$_3$. 
Fig. S5 $^{13}$C NMR spectrum of rac-2a in CDCl$_3$.

Fig. S6 $^{31}$P NMR spectrum of rac-1a in CDCl$_3$. 
2. Photoreaction monitored with UV-vis spectra and $^1$H NMR

2.1. UV-Vis absorption spectral change

![Graph](image1)

**Fig. S7** Changes in the UV-vis absorption spectra of open form (*rac-1a*, blue solid line) to PSS (red dashed line), and closed form (*1b*, red solid line) in toluene ($1.9 \times 10^{-5}$ M).

![Graph](image2)

**Fig. S8** Changes in the UV-Vis absorption spectra of open form (*rac-1a*, blue solid line) to PSS (red dashed line), and closed form (*1b*, red solid line) in methanol ($2.3 \times 10^{-5}$ M).
**Fig. S9** Changes in the UV-Vis absorption spectra of open form (rac-2a, blue solid line) to PSS (red dashed line), and closed form (2b, red solid line) in toluene (2.9 × 10⁻⁵ M).

**Fig. S10** Changes in the UV-Vis absorption spectra of open form (rac-2a, blue solid line) to PSS (red dashed line), and closed form (2b, red solid line) in methanol (2.8 × 10⁻⁵ M).
2.2. \( ^1\text{H} \) NMR spectral change

**Fig. S11** \( ^1\text{H} \) NMR spectrum of photoproducts 1b prepared by UV irradiation to the toluene solution followed by the separated with RP-HPLC (measured in CDCl\(_3\)).

**Fig. S12** \( ^1\text{H} \) NMR spectrum of photoproducts 1b prepared by UV irradiation to the methanol solution followed by the separated with RP-HPLC (measured in CDCl\(_3\)).
**Fig. S13** $^1$H NMR spectrum of photoproducts 2b prepared by UV irradiation to the toluene solution followed by the separated with RP-HPLC (measured in CDCl$_3$).

**Fig. S14** $^1$H NMR spectrum of photoproducts 2b prepared by UV irradiation to the methanol solution followed by the separated with RP-HPLC (measured in CDCl$_3$).
3. Chiral separation

Fig. S15 Chiral HPLC chromatogram of rac-1a in ethanol. (Flow rate: 6 mL / min., Detection wavelength: 254 nm)

Fig. S16 Chiral HPLC chromatogram of a) primary fraction and b) second fraction separated of rac-1a in ethanol, after optical resolution. (Flow rate: 6 mL / min., Detection wavelength: 254 nm)

Fig. S17 Chiral HPLC chromatogram of rac-2a in ethanol. (Flow rate: 6 mL / min., Detection wavelength: 254 nm)
Fig. S18 Chiral HPLC chromatogram of a) primary fraction and b) second fraction separated of rac-2a in ethanol, after optical resolution. (Flow rate: 6 mL / min., Detection wavelength: 254 nm)

Fig. S19 CD spectra for rac-1a of open form in toluene (blue: first fraction, red: second fraction).

Fig. S20 CD spectra at PSS states achieved by UV irradiation to the solution in Fig. S15 in toluene.
Fig. S21 CD spectra for rac-2a of open form in toluene (blue: first fraction, red: second fraction).

Fig. S22 CD spectra at PSS states achieved by UV irradiation to the solution in Fig. S17 in toluene.

Fig. S23 CD spectra for rac-2a of open form in methanol (blue: first fraction, red: second fraction).
**Fig. S24** CD spectra at PSS states achieved by UV irradiation to the solution in **Fig. S19** in methanol.
4. Study in crystalline state

4.1 Photochromism in crystal

**Fig. S25** Photochromism of *rac-1a* in crystal; (a) before and after (b,c) UV irradiation.

**Fig. S26** Photochromism of *rac-2a* in crystal; (a) before and after (b,c) UV irradiation.
Fig. S27 $^1$H NMR spectrum of photoproducts prepared by UV irradiation to single crystals 1a and dissolved in CDCl$_3$.

Fig. S28 $^1$H NMR spectrum of photoproducts prepared by UV irradiation to single crystals 1b and dissolved in CDCl$_3$. 
4.2 X-ray crystallographic data

Table S1. Crystallographic data for rac-1a and rac-2a

<table>
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<tr>
<th>Molecule</th>
<th>rac-1a</th>
<th>rac-2a</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{34}$H$</em>{25}$N$_2$OPS$_2$</td>
<td>C$<em>{36}$H$</em>{26}$N$_3$PS$_3$</td>
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<tr>
<td>Mol weight (g mol$^{-1}$)</td>
<td>572.68</td>
<td>629.79</td>
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<tr>
<td>Crystal dimension (mm)</td>
<td>0.100 × 0.070 × 0.020</td>
<td>0.140 × 0.100 × 0.050</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P2$_1$/c (#14)</td>
<td>P$ar{1}$ (#2)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
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<td>10.0101(2)</td>
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<tr>
<td>$b$ (Å)</td>
<td>29.0720(5)</td>
<td>11.0471(2)</td>
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<tr>
<td>$c$ (Å)</td>
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<td>$\alpha$ (°)</td>
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<td>86.1262(7)</td>
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<tr>
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<tr>
<td>$\gamma$ (°)</td>
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<td>81.5450(7)</td>
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<tr>
<td>$V$ (Å$^3$)</td>
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<td>Z value</td>
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<td>$D_{calc}$ (g mol$^{-1}$)</td>
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<tr>
<td>$wR_2$ [$I &gt; 2\sigma(I)$]</td>
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<td>0.1026</td>
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<tr>
<td>CCDC No.</td>
<td>CCDC-1445542</td>
<td>CCDC-1445543</td>
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5. Computational data

Optimization of molecular conformations of 1a and 2a were carried out by DFT calculation with ωB97XD/6-31G(d,p) level.

5.1. Optimization of molecular conformation

![Optimized structure](image1)

**Fig. S29** Optimized structure of $S_{P-P-1a}$.

![Optimized structure](image2)

**Fig. S30** Optimized structure of $S_{P-M-1a}$. 
Fig. S31 Optimized structure of $R\text{P-}P\text{-}1\text{a}$.  
N-P distance : 3.261 Å  
N-O distance : 3.366 Å  
CH/$\pi$ : 2.500 Å  
C-C distance : 3.564 Å  
CH/$\pi$ : 3.115 Å  
CH/N : 2.500 Å  

Fig. S32 Result of optimization of $R\text{P-M-}1\text{a}$.  
N-P distance : 3.238 Å  
N-O distance : 3.726 Å  
CH/$\pi$ : 3.036 Å  
C-C distance : 3.563 Å  
CH/N : 2.488 Å  
CH/$\pi$ : 3.093 Å
Fig. S33 Optimized structure of \( S_{P-P-2a} \).

Fig. S34 Optimized structure of \( S_{P-M-2a} \).
Fig. S35 Optimized structure of *R*-P-2a.

- **N-P distance**: 3.332 Å
- **CH/N**: 2.505 Å
- **N-S distance**: 3.657 Å
- **C-C distance**: 3.590 Å
- **CH/π**: 6.311 Å

Fig. S36 Optimized structure of *R*-M-2a.

- **N-P distance**: 3.112 Å
- **N-S distance**: 3.804 Å
- **CH/π**: 3.552 Å
- **CH/N**: 2.538 Å
- **C-C distance**: 3.548 Å
- **CH/π**: 3.193 Å
- **CH/π**: 3.465 Å
5.2. Energy difference between $P$- and $M$-conformers estimated by DFT

Fig. S37 Diagram of energy difference between $S_P$-$P$-$1a$ and $S_P$-$M$-$1a$ optimized by oB97XD/6-31G(d,p) level of DFT calculation.
**Fig. S38** Diagram of energy difference between $S_{P}-P$-2a and $S_{P}-M$-2a optimized by oB97XD/6-31G(d,p) level of DFT calculation.

**Fig. S39** Diagram of energy difference between diastereomers of $S_{P}-(R,R)$-1b and $S_{P}-(S,S)$-1b calculated by CAM-B3LYP/6-31G(d,p) level of DFT calculation.
6. Other NMR data

![Fig. S40 1H NMR spectrum of rac-1a in toluene-d8.](image)

![Fig. S41 1H NMR spectrum of rac-2a in toluene-d8.](image)
Fig. S42 $^{31}$P NMR spectrum of rac-1a in toluene-$d_8$. 
Fig. S43 $^{31}$P NMR spectrum of rac-2a in toluene-$d_8$. 