Visible Light Photoredox Catalyzed Thiophosphate Synthesis Using Methylene Blue as Promoter

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1 Preparation of Substrates

1) Preparation of the phosphine oxides

The secondary phosphines were prepared by a procedure analogous to the one reported by Gessner et al. in 2014.¹

\[ \text{R-Br} \xrightarrow{\text{Mg, THF, r.t., Ar}} \text{R-MgBr} \xrightarrow{\text{EtO\(\cdot\)PO\(\cdot\)H, THF, 0°C, Ar}} \text{R-P=O} \]

\( R = \text{aryl, alkyl} \)

**Di-p-tolylphosphine oxide (4b)**

1.3g. 39% yield. Colourless solid, m.p. 98-99°C. \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm): \( \delta 8.03 (d, J = 478.0 \text{ Hz, 1H}), 7.60-7.54 (m, 4H), 7.30-7.26 (m, 4H), 2.40 (s, 6H). \) The data matched the reported.²

**Bis(4-methoxyphenyl)phosphine oxide (4c)**

2.8g. 85% yield. Colourless solid, m.p. 146-148°C. \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm): \( \delta 8.04 (d, J = 481.2 \text{ Hz, 1H}), 7.62-7.57 (m, 4H), 6.99-6.97 (m, 4H), 3.83 (s, 6H). \) The data matched the reported.²

**Diisopropylphosphine oxide (4d)**

1.7g. 65% yield. Colorless oil. \(^1^H\) NMR (400 MHz, CDCl\(_3\), ppm): \( \delta 6.36 (d, J = 8.1 \)
Hz, 2H), 2.06-2.00 (m, 2H), 1.249-1.19 (m, 12H). The data matched the reported. 3

Dicyclohexylphosphine oxide (4e)

![Dicyclohexylphosphine oxide](image)

2.8g, 80% yield. colourless solid, m.p. 71-73°C. 1H NMR (400 MHz, CDCl3, ppm): δ 6.29 (d, J = 434.3 Hz, 1H), 2.00-1.21 (m, 22H). The data matched the reported. 4

2 Photoredox Dehydrogenative Coupling Reaction

2.1 Optimization of the Photocatalyst and Light Source

A dry tube equipped with a stirring bar was charged with 4-chlorothiophenol (1a) (72.3 mg, 0.5 mmol, 1.0 equiv.) and diethyl phosphonate (2a) (207.15 mg, 1.5 mmol, 3.0 equiv.), the photocatalyst (PC) (3.0 mol%) and K2CO3 (1.0 equiv.). The solvent 1PrOH (1.0 mL) were added, the tube was sealed and the mixture was stirred under irradiation for 24 hour in front of the appropriate light source. H2O (2 mL) and EtOAc (4 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried with MgSO4, filtered and evaporated. Triphenylphosphine (65.6 mg, 0.25 mmol, 0.5 equiv.) and CDCl3 (0.5 mL) were added and the mixture was analysed by 31P NMR spectroscopy to determine the NMR yield.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Light Source</th>
<th>λ (nm)</th>
<th>Yield(^a) (%)</th>
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<tbody>
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<td>1</td>
<td>PC 1</td>
<td>blue LEDs</td>
<td>455</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
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<td>75</td>
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<td>3</td>
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<td>51</td>
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<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>PC 5</td>
<td>blue LEDs</td>
<td>455</td>
<td>40</td>
</tr>
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<td>6</td>
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<td>35</td>
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<td>50</td>
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<tr>
<td>8</td>
<td>PC 8</td>
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<td>blue LEDs</td>
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<td>80</td>
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<tr>
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<td>green LEDs</td>
<td>530</td>
<td>n.r.</td>
</tr>
<tr>
<td>11(^b)</td>
<td>PC 1</td>
<td>white LEDs</td>
<td>/</td>
<td>20</td>
</tr>
<tr>
<td>12(^c)</td>
<td>PC 1</td>
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<td>310</td>
<td>n.r.</td>
</tr>
<tr>
<td>13(^d)</td>
<td>PC 1</td>
<td>none</td>
<td>/</td>
<td>n.r.</td>
</tr>
<tr>
<td>14</td>
<td>none</td>
<td>blue LED</td>
<td>455</td>
<td>n.r.</td>
</tr>
</tbody>
</table>

\(^a\)\(^3\)P NMR yield using triphenylphosphine as an internal standard. \(^b\)The reaction mixture was irradiated with 15 W green LEDs or 15 W white LEDs. \(^c\)The reaction mixture in a common glass flask was irradiated with 1000 W UV light (\(λ = 310\) nm). \(^d\)The reaction was in dark. PC = photocatalyst, LED = light-emitting diode, n.r. = no reaction.
2.2 Picture of Reaction Set-Up
2.3 Optimization of Reaction Conditions

A dry tube equipped with a stirring bar was charged with 4-chlorothiophenol (1a) (72.3 mg, 0.5 mmol, 1.0 equiv.) and diethyl phosphonate (2a) (207.15 mg, 1.5 mmol, 3.0 equiv.), the methylene blue (MB) (3.0 mol%) and the base (1.0 equiv.). The solvent (1.0 mL) were added, the tube was sealed and the mixture was stirred under irradiation for 12-48 hours in front of the appropriate light source. H2O (2 mL) and EtOAc (4 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (2×2 mL). The combined organic layers were dried with MgSO4, filtered and evaporated.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (equiv)</th>
<th>Solvent</th>
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<th>Yield (%)</th>
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<td>48</td>
<td>N.R.</td>
</tr>
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<tr>
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<td>DBU</td>
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<td>2PrOH</td>
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<tr>
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<td>K2CO3</td>
<td>2PrOH: MeCN (4:1)</td>
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<td>91</td>
</tr>
<tr>
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<td>19</td>
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<td>53</td>
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</table>
2.4 Substrate Scope.

2.4.1 Substrate Scope A:

![Chemical Reaction and Structures]

3b, R = H, 87%, 24h
3c, R = Me, 92%, 24h
3d, R = OMe, 86%, 24h
3e, R = Bu, 61%, 24h
3f, X = Cl, 95%, 24h
3g, X = Br, 92%, 24h
3h, R¹ = R² = Me, 20%, 72h
3i, R¹ = R² = Pr, 60%, 24h
3j, R¹ = R² = Bu, 37%, 48h
3k, 71%, 24h
3l, 85%, 24h
3m, 67%, 24h
3n, 73%, 24h
3o, 85%, 24h
3p, 42%, 48h
3q, 54%, 48h
3r, 43%, 48h
3s, 45%, 48h
3t, 67%, 24h
3u, 83%, 24h
3v, 76%, 24h
3w, 55%, 36h
3x, 64%, 24h
3y, 45%, 48h
3z, 93%, 24h
3aa, 80%, 24h

2.4.2 Substrate Scope B:
2.4.3 The Characterization Data of the Products

**S-(4-chlorophenyl) O, O-diethyl phosphorothioate (3a)**

Prepared according to general procedure, the reaction of 4-chlorobenzentheniol 1a (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^t$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 133.3 mg (95%) of 3a as colorless oil.

**$^1$H NMR (600 MHz, CDCl$_3$, ppm):** $\delta$ 7.50-7.49 (m, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 4.24-4.12 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H). **$^{13}$C NMR (100 MHz, CDCl$_3$, ppm):** $\delta$ 135.8 (d, $J = 5.3$ Hz), 135.5 (d, $J = 3.6$ Hz), 129.6 (d, $J = 2.2$ Hz), 125.2 (d, $J = 7.1$ Hz), 64.3 (d, $J = 6.1$ Hz), 16.1 (d, $J = 7.1$ Hz). **$^{31}$P NMR (162 MHz, CDCl$_3$, ppm):** $\delta$ 22.1.

**HR-MS (ESI):** $m/z$ calculated for C$_{10}$H$_{14}$ClO$_3$PS [M+Na]$^+$: 302.9987, found: 302.9987.

**O, O-diethyl S-phenyl phosphorothioate (3b)**
Prepared according to general procedure, the reaction of benzenethiol 1b (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 107.1 mg (87%) of 3b as yellow oil. 

1H NMR (400 MHz, CDCl₃, ppm): δ 7.58-7.56 (m, 2H), 7.35 (d, J = 5.2 Hz, 3H), 4.25-4.14 (m, 4H), 1.31 (t, J = 6.9 Hz, 6H).

13C NMR (150 MHz, CDCl₃, ppm): δ 134.6 (d, J = 5.3 Hz), 129.4 (d, J = 2.2 Hz), 129.0 (d, J = 2.8 Hz), 126.6 (d, J =7.1 Hz), 64.1 (d, J = 5.8 Hz), 16.1 (d, J = 7.1 Hz).

31P NMR (162 MHz, CDCl₃, ppm): δ 22.9.


O, O-diethyl S-(p-tolyl) phosphorothioate (3c)

Prepared according to general procedure, the reaction of 4-methylbenzenethiol 1c (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 119.7 mg (92%) of 3c as colorless oil.

1H NMR (600 MHz, CDCl₃, ppm): δ 7.44-7.41 (m, 2H), 7.15 (d, J = 7.8 Hz, 2H), 4.23-4.14 (m, 4H), 2.34 (s, 3H), 1.31 (t, J = 7.1 Hz, 6H).

13C NMR (100 MHz, CDCl₃, ppm): δ 139.3 (d, J = 3.1 Hz), 134.6 (d, J = 5.3 Hz), 130.2 (d, J = 2.5 Hz), 122.8 (d, J =7.2 Hz), 64.0 (d, J = 5.0 Hz), 21.2, 16.1 (d, J = 7.2 Hz).

31P NMR (162 MHz, CDCl₃, ppm): δ 23.3.

HR-MS (ESI): m/z calculated for C₁₁H₁₇O₃PS [M+Na]⁺: 283.0534, found: 283.0531.

O, O-diethyl S-(4-methoxyphenyl) phosphorothioate (3d)

Prepared according to general procedure, the reaction of 4-methoxybenzenethiol 1d (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 91.1 mg (66%) of 3d as colorless oil.

S9
$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.46 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 4.24-4.10 (m, 4H), 3.80 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): $\delta$ 160.4 (d, $J = 2.0$ Hz), 136.3 (d, $J = 4.7$ Hz), 116.6 (d, $J = 7.2$ Hz), 114.9 (d, $J = 2.3$ Hz), 63.9 (d, $J = 6.2$ Hz), 55.3, 16.6 (d, $J = 7.0$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 23.5.

HR-MS (ESI): $m/z$ calculated for C$_{11}$H$_{17}$O$_4$PS [M+Na]$^+$: 299.0483, found: 299.0479.

S-(4-(tert-butyl)phenyl) O, O-diethyl phosphorothioate (3e)$^5$

Prepared according to general procedure, the reaction of 4-(tert-butyl)benzenethiol 1e (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.2 mg (61%) of 3e as colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.48 (dd, $J = 8.5$ Hz, $J = 2.1$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 4.26-4.14 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 152.3 (d, $J = 5.1$ Hz), 134.3 (d, $J = 3.1$ Hz), 126.4 (d, $J = 5.2$ Hz), 122.8 (d, $J = 7.2$ Hz), 63.9 (d, $J = 6.0$ Hz), 34.6, 31.1, 16.0 (d, $J = 7.1$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 23.3.

HR-MS (ESI): $m/z$ calculated for C$_{10}$H$_{14}$BrO$_3$PS [M+Na]$^+$: 325.1003, found: 325.1002.

S-(4-bromophenyl) O, O-diethyl phosphorothioate (3f)$^7$

Prepared according to general procedure, the reaction of 4-bromobenzanethiol 1f (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 149.7 mg (92%) of 3f as colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): $\delta$ 7.48-7.42 (m, 4H), 4.24-4.14 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 136.1 (d, $J = 5.1$ Hz), 132.6 (d, $J = 2.1$ Hz), 126.0 (d, $J = 7.0$ Hz), 123.7 (d, $J = 3.6$ Hz), 64.4 (d, $J = 6.4$ Hz), 16.1 (d, $J = 7.2$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 21.9.

HR-MS (ESI): $m/z$ calculated for C$_{10}$H$_{14}$BrO$_3$PS [M+Na]$^+$: 346.9482, found: 346.9480.
**O, O-diethyl S-(4-fluorophenyl) phosphorothioate (3g)**

![Chemical structure of 3g](image)

Prepared according to general procedure, the reaction of 4-fluorobenzenethiol 1g (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^i$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 84.5 mg (64%) of 3g as colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.58-7.50 (m, 2H), 7.05 (t, J = 8.4 Hz, 2H), 4.26-4.10 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H).
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 163.3 (dd, J = 248.3 Hz, J = 3.1 Hz), 136.7 (dd, J = 8.4 Hz, J = 4.9 Hz), 121.7 (dd, J = 7.1 Hz, J = 3.4 Hz), 116.6 (dd, J = 22.0 Hz, J = 2.1 Hz), 64.2 (d, J = 6.1 Hz), 16.1 (d, J = 7.1 Hz).
$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 22.6 (d, J = 5.0 Hz).

HR-MS (ESI): m/z calculated for C$_{10}$H$_{14}$FO$_3$PS [M+Na]$^+$: 287.0283, found: 287.0287.

**S-(4-chlorophenyl) O, O-dimethyl phosphorothioate (3h)**

![Chemical structure of 3h](image)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), dimethyl phosphonate 2b (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^i$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 72h, afforded 25.2 mg (20%) of 3h as colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.50 (dd, J = 8.6 Hz, J = 2.1 Hz, 2H), 7.38-7.31 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 135.7 (d, J = 5.2 Hz), 135.6 (d, J = 1.9 Hz), 129.6 (d, J = 2.3 Hz), 124.5 (d, J = 7.0 Hz), 54.3 (d, J = 6.4 Hz).
$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 25.4.

HR-MS (ESI): m/z calculated for C$_{8}$H$_{10}$ClO$_3$PS [M+Na]$^+$: 274.9674, found: 274.9673.

**S-(4-chlorophenyl) O, O-diisopropyl phosphorothioate (3i)**

![Chemical structure of 3i](image)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), diisopropyl phosphonate 2c (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^i$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 72h, afforded 12.4 mg (10%) of 3i as colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.49-7.43 (m, 2H), 7.34-7.29 (m, 2H), 4.15-4.07 (m, 4H), 1.16-1.07 (d, J = 6.7 Hz, 12H), 1.07-1.00 (d, J = 6.7 Hz, 12H).
$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 135.7 (d, J = 5.2 Hz), 135.6 (d, J = 1.9 Hz), 129.6 (d, J = 2.3 Hz), 124.5 (d, J = 7.0 Hz), 54.3 (d, J = 6.4 Hz).
$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 25.4.

HR-MS (ESI): m/z calculated for C$_{10}$H$_{18}$ClO$_3$PS [M+Na]$^+$: 276.9972, found: 276.9970.
dimethyl phosphonate 2c (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in ¹PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.6 mg (60%) of 3i as colorless oil.

¹H NMR (600 MHz, CDCl₃, ppm): δ 7.53 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 4.81-4.71 (m, 2H), 1.33 (d, J = 6.2 Hz, 6H), 1.27 (d, J = 6.2 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ 135.4 (d, J = 5.4 Hz), 135.1 (d, J = 3.4 Hz), 129.3 (d, J = 2.0 Hz), 125.9 (d, J = 6.9 Hz), 73.5 (d, J = 6.8 Hz), 23.8 (d, J = 4.1 Hz), 23.5 (d, J = 5.6 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 19.6. HR-MS (ESI): m/z calculated for C₁₂H₁₈ClO₃PS [M+Na]⁺: 331.0300, found: 331.0301.

O, O-diisopropyl S-(4-chlorophenyl) phosphorothioate (3j)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), diisopropyl phosphonate 2d (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in ¹PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 62.3 mg (37%) of 3j as colorless oil.

¹H NMR (600 MHz, CDCl₃, ppm): δ 7.53 (d, J = 6.9 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 1.47 (s, 18H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ 135.4 (d, J = 5.4 Hz), 134.8 (d, J = 3.4 Hz), 129.0 (d, J = 1.9 Hz), 127.4 (d, J = 7.8 Hz), 85.4 (d, J = 9.5 Hz), 30.1 (d, J = 4.3 Hz). ³¹P NMR (162 MHz, CDCl₃, ppm): δ 12.1. HR-MS (ESI): m/z calculated for C₁₄H₂₂ClO₃PS [M+Na]⁺: 359.0613, found: 359.0608.

O, O-diisopropyl S-(p-tolyl) phosphorothioate (3k)

Prepared according to general procedure, the reaction of 4-methylbenzenethiol 1c (0.5 mmol), diisopropyl phosphonate 2c (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in ¹PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 102.3 mg (71%) of 3k as colorless oil.

¹H NMR (600 MHz, CDCl₃, ppm): δ 7.47 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 4.79-4.73 (m, 2H), 2.34 (s, 3H), 1.30 (dd, J = 39.3 Hz, J = 6.3 Hz, 12H). ¹³C NMR (150 MHz, CDCl₃, ppm): δ 138.8 (d, J = 3.0 Hz), 134.3 (d, J = 5.4 Hz), 129.9
(d, \( J = 2.3 \) Hz), 123.5 (d, \( J = 7.3 \) Hz), 73.2 (d, \( J = 6.6 \) Hz), 23.8 (d, \( J = 4.1 \) Hz), 23.5 (d, \( J = 5.7 \) Hz), 21.2. \(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \( \delta \) 20.8.

**HR-MS (ESI):** \( m/z \) calculated for C\(_{13}\)H\(_{21}\)O\(_3\)PS [M+Na]^+: 311.0847, found: 311.0854.

**O, O-dicyclohexyl S-(p-tolyl) phosphorothioate (3l)**

\[
\begin{align*}
\text{Me} & \\
\text{O} & \text{P} & \text{O} & \text{Cy} \\
\text{S} & \text{O} & \text{P} & \text{O} & \text{Cy}
\end{align*}
\]

Prepared according to general procedure, the reaction of 4-methylbenzenethiol 1c (0.5 mmol), dicyclohexyl phosphonate 2e (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \( \text{\textsuperscript{i}PrOH} \) (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 156.6 mg (85%) of 3l as colorless oil.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\), ppm): \( \delta \) 7.48-7.45 (m, 2H), 7.13 (d, \( J = 7.9 \) Hz, 2H), 4.52-4.43 (m, 2H), 2.33 (s, 3H), 1.93-1.82 (m, 4H), 1.73-1.67 (m, 4H), 1.57-1.42 (m, 6H), 1.36-1.18 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \( \delta \) 138.8 (d, \( J = 2.9 \) Hz), 134.4 (d, \( J = 5.2 \) Hz), 130.0 (d, \( J = 2.2 \) Hz), 123.7 (d, \( J = 7.0 \) Hz), 77.9 (d, \( J = 7.0 \) Hz), 33.4 (dd, \( J = 30.0, J = 4.3 \) Hz), 25.1, 23.6 (d, \( J = 1.3 \) Hz), 21.2. \(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \( \delta \) 20.8.

**HR-MS (ESI):** \( m/z \) calculated for C\(_{19}\)H\(_{29}\)O\(_3\)PS [M+Na]^+: 391.1473, found: 391.1475.

**S-(4-aminophenyl) O, O-diethyl phosphorothioate (3m)**

\[
\begin{align*}
\text{H}_2\text{N} & \\
\text{S} & \text{O} & \text{P} & \text{O} & \text{Et} \\
\text{O} & \text{P} & \text{O} & \text{Et}
\end{align*}
\]

Prepared according to general procedure, the reaction of 4-aminobenzenethiol 1m (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \( \text{\textsuperscript{i}PrOH} \) (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 87.5 mg (67%) of 3m as colorless oil.

\(^{1}\)H NMR (600 MHz, CDCl\(_3\), ppm): \( \delta \) 7.30 (d, \( J = 7.8 \) Hz, 2H), 6.63 (d, \( J = 8.1 \) Hz, 2H), 4.22-4.11 (m, 4H), 3.76 (br s, 2H), 1.31 (t, \( J = 7.1 \) Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\), ppm): \( \delta \) 147.7 (d, \( J =2.3 \) Hz), 136.4 (d, \( J = 4.5 \) Hz), 115.8 (d, \( J = 2.2 \) Hz), 113.0 (d, \( J = 7.3 \) Hz), 63.9 (d, \( J = 6.2 \) Hz), 16.2 (d, \( J = 7.2 \) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \( \delta \) 23.8.

**HR-MS (ESI):** \( m/z \) calculated for C\(_{10}\)H\(_{16}\)O\(_3\)PS [M+Na]^+: 284.0486, found: 284.0504.
O, O-diethyl S-(4-hydroxyphenyl) phosphorothioate (3n)\(^7\)

![Chemical structure of 3n](image)

Prepared according to general procedure, the reaction of 4-mercaptophenol 1n (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \(^i\)PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 95.7 mg (73%) of 3n as colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 8.61 (s, 1H), 7.32-7.27 (m, 2H), 6.62 (d, \(J = 8.4\) Hz, 2H), 4.27-4.13 (m, 4H), 1.35 (t, \(J = 7.1\) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 158.6 (d, \(J = 3.1\) Hz), 136.8 (d, \(J = 4.8\) Hz), 117.2 (d, \(J = 2.7\) Hz), 113.2 (d, \(J = 7.1\) Hz), 64.7 (d, \(J = 6.8\) Hz), 16.2 (d, \(J = 6.9\) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \(\delta\) 25.1.

HR-MS (ESI): \(m/z\) calculated for C\(_{10}\)H\(_{15}\)O\(_4\)PS [M+Na]\(^+\): 285.0326, found: 285.0327.

S-(4-chlorophenyl) O, O-dicyclohexyl phosphorothioate (3o)

![Chemical structure of 3o](image)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), dicyclohexyl phosphonate 2e (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \(^i\)PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 165.2 mg (85%) of 3o as colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\), ppm): \(\delta\) 7.53 (d, \(J = 8.2\) Hz, 2H), 7.30 (d, \(J = 8.1\) Hz, 2H), 4.49 (m, 2H), 1.93-1.82 (m, 4H), 1.72-1.68 (m, 4H), 1.54-1.47 (m, 6H), 1.32-1.22 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 135.4 (d, \(J = 5.4\) Hz), 135.0 (d, \(J = 3.1\) Hz), 129.3 (d, \(J = 2.0\) Hz), 126.0 (d, \(J = 7.0\) Hz), 78.2 (d, \(J = 6.8\) Hz), 33.3 (dd, \(J = 27.4\) Hz, \(J = 4.1\) Hz), 25.0, 23.4 (d, \(J = 1.2\) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \(\delta\) 19.6.

HR-MS (ESI): \(m/z\) calculated for C\(_{18}\)H\(_{26}\)ClO\(_3\)PS [M+Na]\(^+\): 411.0926, found: 411.0929.

O, O-diethyl S-(4-nitrophenyl) phosphorothioate (3p)\(^7\)

![Chemical structure of 3p](image)
Prepared according to general procedure, the reaction of 4-nitrobenzenethiol 1p (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 61.1 mg (42%) of 3p as colorless oil.

**1H NMR (600 MHz, CDCl₃, ppm):** δ 8.20 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.3 Hz, 2H), 4.32-4.16 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H).

**13C NMR (100 MHz, CDCl₃, ppm):** δ 147.8 (d, J = 2.1 Hz), 136.2 (d, J = 6.5 Hz), 134.1 (d, J = 5.9 Hz), 124.1 (d, J = 1.5 Hz), 64.7 (d, J = 6.4 Hz), 16.0 (d, J = 7.0 Hz).

**31P NMR (162 MHz, CDCl₃, ppm):** δ 20.1.

**HR-MS (ESI):** m/z calculated for C₁₀H₁₄NO₅PS [M+Na]⁺: 314.0228, found: 314.0246.

**S-(2-bromophenyl) O, O-diethyl phosphorothioate (3q)**

Prepared according to general procedure, the reaction of 2-bromobenzenethiol 1q (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 87.7 mg (54%) of 3q as colorless oil.

**1H NMR (600 MHz, CDCl₃, ppm):** δ 7.79 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 4.28-4.17 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H).

**13C NMR (100 MHz, CDCl₃, ppm):** δ 136.5 (d, J = 4.1 Hz), 133.6 (d, J = 1.9 Hz), 130.3 (d, J = 2.5 Hz), 128.7 (d, J = 6.1 Hz), 128.5 (d, J = 7.4 Hz), 128.2 (d, J = 2.2 Hz), 64.5 (d, J = 6.2 Hz), 16.1 (d, J = 7.2 Hz).

**31P NMR (162 MHz, CDCl₃, ppm):** δ 21.2.

**HR-MS (ESI):** m/z calculated for C₁₀H₁₄BrO₃PS [M+Na]⁺: 346.9482, found: 346.9481.

**S-(2-aminophenyl) O, O-diethyl phosphorothioate (3r)**

Prepared according to general procedure, the reaction of 2-aminobenzenethiol 1r (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in
PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48 h, afforded 56.1 mg (43%) of 3r as colorless oil.

\[ \text{1H NMR (600 MHz, CDCl}_3, \text{ ppm): } \delta 7.38 (d, J = 7.8 \text{ Hz}, 1H), 7.17 (t, J = 7.8 \text{ Hz}, 1H), 6.74 (d, J = 8.1 \text{ Hz}, 1H), 6.70 (t, J = 7.6 \text{ Hz}, 1H), 4.58-3.79 (br s, 2H), 4.21-4.12 (m, 4H), 1.30 (t, J = 7.1 \text{ Hz}, 6H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3, \text{ ppm): } \delta 149.4 (d, J = 4.3 \text{ Hz}), 137.3 (d, J = 4.3 \text{ Hz}), 131.0 (d, J = 3.2 \text{ Hz}), 118.6 (d, J = 2.7 \text{ Hz}), 115.8 (d, J = 2.8 \text{ Hz}), 108.0 (d, J = 7.3 \text{ Hz}), 64.4 (d, J = 6.8 \text{ Hz}), 16.0 (d, J = 6.8 \text{ Hz}). \]

\[ \text{31P NMR (162 MHz, CDCl}_3, \text{ ppm): } \delta 22.8. \]

HR-MS (ESI): \( m/z \) calculated for \( \text{C}_{10}\text{H}_{16}\text{NO}_3\text{PS}[\text{M+Na}]^+: \) 284.0486, found: 284.0486.

S-(4-cyanophenyl) O, O-diethyl phosphorothioate (3s)

Prepared according to general procedure, the reaction of methyl 4-mercaptobenzonitrile 1s (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and \( \text{K}_2\text{CO}_3 \) (0.5 mmol) in \( ^{i}\text{PrOH} \) (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48 h, afforded 61.0 mg (45%) of 3s as colorless oil.

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm): } \delta 7.69 (d, J = 8.1 \text{ Hz}, 2H), 7.61 (d, J = 8.1 \text{ Hz}, 2H), 4.26-4.13 (m, 4H), 1.31 (t, J = 7.1 \text{ Hz}, 6H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3, \text{ ppm): } \delta 134.3 (d, J = 5.8 \text{ Hz}), 134.0 (d, J = 6.7 \text{ Hz}), 132.7 (d, J = 1.7 \text{ Hz}), 118.1 (d, J = 1.5 \text{ Hz}), 112.5 (d, J = 2.2 \text{ Hz}), 64.7 (d, J = 6.4 \text{ Hz}), 16.1 (d, J = 6.9 \text{ Hz}). \]

\[ \text{31P NMR (162 MHz, CDCl}_3, \text{ ppm): } \delta 20.4. \]

HR-MS (ESI): \( m/z \) calculated for \( \text{C}_{11}\text{H}_{14}\text{NO}_3\text{PS}[\text{M+Na}]^+: \) 294.0330, found: 294.0333.

O, O-diethyl S-(naphthalen-2-yl) phosphorothioate (3t)

Prepared according to general procedure, the reaction of naphthalene-2-thiol 1t (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and \( \text{K}_2\text{CO}_3 \) (0.5 mmol) in \( ^{i}\text{PrOH} \) (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24 h, afforded 99.2 mg (67%) of 3t as colorless oil.

\[ \text{1H NMR (400 MHz, CDCl}_3, \text{ ppm): } \delta 8.09 (s, 1H), 7.85-7.77 (m, 3H), 7.61 (d, J = 8.6 \text{ Hz}, 1H), 7.55-7.47 (m, 2H), 4.29-4.15 (m, 4H), 1.31 (t, J = 7.1 \text{ Hz}, 6H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3, \text{ ppm): } \delta 139.6 (d, J = 6.8 \text{ Hz}), 125.5 (d, J = 3.2 \text{ Hz}), 123.1 (d, J = 1.7 \text{ Hz}), 119.3 (d, J = 3.2 \text{ Hz}), 64.7 (d, J = 6.8 \text{ Hz}), 16.1 (d, J = 6.9 \text{ Hz}). \]

HR-MS (ESI): \( m/z \) calculated for \( \text{C}_{12}\text{H}_{16}\text{NO}_3\text{PS}[\text{M+Na}]^+: \) 304.0486, found: 304.0486.

O, O-diethyl S-(naphthalen-2-yl) phosphorothioate (3t)
(100 MHz, CDCl$_3$, ppm): δ 134.3 (d, $J = 6.8$ Hz), 133.5 (d, $J = 2.1$ Hz), 133.0 (d, $J = 1.5$ Hz), 130.9 (d, $J = 4.0$ Hz), 128.9 (d, $J = 1.7$ Hz), 127.7 (d, $J = 1.2$ Hz), 127.6 (d, $J = 0.9$ Hz), 127.0 (d, $J = 1.4$ Hz), 126.7 (d, $J = 0.8$ Hz), 123.7 (d, $J = 7.5$ Hz), 64.1 (d, $J = 5.8$ Hz), 16.0 (d, $J = 7.2$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 22.8.

HR-MS (ESI): $m/z$ calculated for C$_{14}$H$_{17}$O$_3$PS [M+Na]$^+$: 319.0534, found: 319.0535.

5,5-dimethyl-2-(naphthalen-2-ylthio)-1,3,2-dioxaphosphinane 2-oxide (3u)

Prepared according to general procedure, the reaction of naphthalene-2-thiol 1t (0.5 mmol), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide 2f (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 127.9 mg (83%) of 3u as white solid, m.p. 100-102°C.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 8.15 (s, 1H), 7.83-7.80 (m, 3H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.52-7.49 (m, 2H), 4.26-4.23 (m, 2H), 3.99-3.89 (m, 2H), 1.28 (s, 3H), 0.87 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 134.6 (d, $J = 6.7$ Hz), 133.7 (d, $J = 2.3$ Hz), 133.72 (d, $J = 2.0$ Hz), 130.9 (d, $J = 4.0$ Hz), 129.3 (d, $J = 1.7$ Hz), 127.83 (d, $J = 1.5$ Hz), 127.81 (d, $J = 1.4$ Hz), 127.2 (d, $J = 1.4$ Hz), 126.8 (d, $J = 0.8$ Hz), 122.1 (d, $J = 6.8$ Hz), 78.4 (d, $J = 7.3$ Hz), 32.6 (d, $J = 6.7$ Hz), 21.2 (d, $J = 241.0$ Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 14.6.

HR-MS (ESI): $m/z$ calculated for C$_{15}$H$_{17}$O$_3$PS [M+Na]$^+$: 331.3215, found: 331.0550.

Methyl 4-((diethoxyphosphoryl)thio)benzoate (3v)

Prepared according to general procedure, the reaction of methyl 4-mercaptobenzoate 1v (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 115.6 mg (76%) of 3v as colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 8.00 (d, $J = 8.2$ Hz, 2H), 7.66-7.63 (m, 2H), 4.24-4.16 (m, 4H), 3.92 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 166.4 (s), 133.8 (d, $J = 5.6$ Hz), 133.0 (d, $J = 6.8$ Hz), 130.4 (d, $J = 2.5$ Hz), 130.3 (d, $J = 1.9$ Hz), 64.4 (d, $J = 6.2$ Hz), 52.4 (s), 16.1 (d, $J = 7.1$ Hz). $^{31}$P
NMR (162 MHz, CDCl₃, ppm): δ 21.3.
HR-MS (ESI): m/z calculated for C₁₂H₁₇O₅PS [M+Na]⁺: 327.0432, found: 327.0435.

*O, O-diethyl S-(4-(2,2,2-trifluoroacetamido)phenyl) phosphorothioate (3w)*

![Chemical structure](image)

Prepared according to general procedure, the reaction of 2,2,2-trifluoro-N-(4-mercaptophenyl)acetamide 1w (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 98.2 mg (55%) of 3w as yellow oil.

¹H NMR (400 MHz, CDCl₃, ppm): δ 9.97 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.47 (dd, J = 8.7 Hz, J = 2.2 Hz, 2H), 4.28-4.11 (m, 4H), 1.40-1.31 (m, 6H).

¹³C NMR (100 MHz, CDCl₃, ppm): δ 155.2 (d, J = 3.8 Hz), 137.6 (d, J = 3.1 Hz), 135.5 (d, J = 5.1 Hz), 122.1 (d, J = 6.8 Hz), 121.7 (d, J = 1.6 Hz), 117.5 (d, J = 286.3 Hz), 64.7 (dd, J = 10.5 Hz, J = 3.6 Hz), 16.2 (dd, J = 30.1 Hz, J = 6.7 Hz).

³¹P NMR (162 MHz, CDCl₃, ppm): δ 22.7.

HR-MS(ESI): m/z calculated for C₁₂H₁₅F₃NO₄PS [M+Na]⁺: 380.0309, found: 380.0319.

*O, O-diethyl S-(furan-2-ylmethyl) phosphorothioate (3x)*

![Chemical structure](image)

Prepared according to general procedure, the reaction of furan-2-ylmethanethiol 1x (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K₂CO₃ (0.5 mmol) in iPrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 80.0 mg (64%) of 3x as colorless oil.

¹H NMR (600 MHz, CDCl₃, ppm): δ 7.37 (s, 1H), 6.36-6.25 (m, 2H), 4.19-4.04 (m, 6H), 1.33 (t, J = 7.0 Hz, 6H).

¹³C NMR (150 MHz, CDCl₃, ppm): δ 150.2 (d, J = 4.6 Hz), 142.5, 110.6, 108.4, 63.6 (d, J = 5.6 Hz), 27.2 (d, J = 3.8 Hz), 15.9 (d, J = 7.2 Hz).

³¹P NMR (162 MHz, CDCl₃, ppm): δ 26.2.


*O, O-diethyl S-(3-methoxyphenyl) phosphorothioate (3y)*
Prepared according to general procedure, the reaction of 3-methoxybenzenethiol 1y (0.5 mmol), diethyl phosphonate 2a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^4$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 62.1 mg (45%) of 3y as colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.25 (d, $J$ = 8.0 Hz, 1H), 7.18-7.10 (m, 2H), 6.90 (d, $J$ = 8.3 Hz, 1H), 4.24-4.15 (m, 4H), 3.81 (s, 3H), 1.32 (t, $J$ = 7.1 Hz, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 159.9 (d, $J$ = 1.6 Hz), 130.1 (d, $J$ = 2.2 Hz), 127.6 (d, $J$ = 7.0 Hz), 126.7 (d, $J$ = 5.4 Hz), 119.7 (d, $J$ = 5.3 Hz), 115.1 (d, $J$ = 2.7 Hz), 64.2 (d, $J$ = 5.6 Hz), 55.4, 16.1 (d, $J$ = 7.2 Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 22.7.

HR-MS (ESI): m/z calculated for C$_{11}$H$_{17}$O$_4$PS [M+Na]$^+$: 299.0483, found: 299.0483.

$S$-((2-aminophenyl)O, $O$-dicyclohexyl phosphorothioate (3z)

Prepared according to general procedure, the reaction of 2-aminobenzenethiol 1r (0.5 mmol), dicyclohexyl phosphonate 2e (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^4$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 171.7 mg (93%) of 3z as pale yellow solid, m.p. 90-92°C.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.43 (d, $J$ = 7.8 Hz, 1H), 7.17 (t, $J$ = 7.8 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 6.73 (t, $J$ = 7.5 Hz, 1H), 4.59 (br s, 2H), 4.52-4.42 (m, 2H), 1.92-1.78 (m, 4H), 1.76-1.61 (m, 4H), 1.56-1.46 (m, 6H), 1.35-1.18 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 148.6 (d, $J$ = 3.8 Hz), 137.6 (d, $J$ = 4.2 Hz), 131.1 (d, $J$ = 3.0 Hz), 119.5 (d, $J$ = 2.2 Hz), 116.8 (d, $J$ = 2.3 Hz), 110.0 (d, $J$ = 7.9 Hz), 78.5 (d, $J$ = 7.7 Hz), 33.4 (dd, $J$ = 31.1 Hz, $J$ = 4.2 Hz), 25.1, 23.6 (d, $J$ = 0.8 Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 20.9.

HR-MS (ESI): m/z calculated for C$_{18}$H$_{28}$NO$_3$PS [M+Na]$^+$: 392.1425, found: 392.1430.

2-((4-chlorophenyl)thio)-5, 5-dimethyl-1, 3, 2-dioxaphosphinane 2-oxide (3aa)
Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide 2f (1.5 mmol), MB (3 mol%) and K_{2}CO_{3} (0.5 mmol) in \(^{i}\)PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 117.0 mg (80%) of 3aa as white solid, m.p. 130-132°C.

\(^1\)H NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 7.57 (dd, \(J = 8.4\) Hz, \(J = 1.7\) Hz, 2H), 7.33 (d, \(J = 8.4\) Hz, 2H), 4.21 (dd, \(J = 10.8\) Hz, \(J = 3.6\) Hz, 2H), 4.00-3.89 (m, 2H), 1.29 (s, 3H), 0.89 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 136.0 (d, \(J = 5.0\) Hz), 135.8 (d, \(J = 3.2\) Hz), 129.8 (d, \(J = 2.1\) Hz), 123.4 (d, \(J = 6.4\) Hz), 78.4 (d, \(J = 7.1\) Hz), 32.6 (d, \(J = 6.9\) Hz), 21.2 (d, \(J = 158.6\) Hz).

\(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \(\delta\) 14.1.

HR-MS (ESI): \(m/z\) calculated for C\(_{11}\)H\(_{14}\)ClO\(_3\)PS [M+Na]\(^{+}\): 314.9987, found: 314.9990.

\(S\)-(4-chlorophenyl) diphenylphosphinothioate (5a)\(^6\)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), diphenylphosphine oxide 4a (1.5 mmol), MB (3 mol%) and K\(_{2}\)CO\(_3\) (0.5 mmol) in \(^{i}\)PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 148.2 mg (86%) of 5a as white solid, m.p. 95-97°C.

\(^1\)H NMR (600 MHz, CDCl\(_3\), ppm): \(\delta\) 7.85-7.82 (m, 4H), 7.54-7.52 (m, 2H), 7.47-7.44 (m, 4H), 7.38 (d, \(J = 8.1\) Hz, 2H), 7.18 (d, \(J = 8.1\) Hz, 2H).

\(^{13}\)C NMR (150 MHz, CDCl\(_3\), ppm): \(\delta\) 136.6 (d, \(J = 3.8\) Hz), 135.6 (d, \(J = 2.5\) Hz), 132.6 (d, \(J = 2.3\) Hz), 132.3 (d, \(J = 106.5\) Hz), 131.7 (d, \(J = 10.2\) Hz), 129.4 (d, \(J = 1.8\) Hz), 128.7 (d, \(J = 13.2\) Hz), 124.8 (d, \(J = 5.0\) Hz).

\(^{31}\)P NMR (162 MHz, CDCl\(_3\), ppm): \(\delta\) 41.5.

HR-MS (ESI): \(m/z\) calculated for C\(_{18}\)H\(_{14}\)ClOPS [M+Na]\(^{+}\): 367.0089, found: 367.0097.

\(S\)-(p-tolyl) diphenylphosphinothioate (5b)\(^{11}\)
Prepared according to general procedure, the reaction of 4-methylbenzenethiol 1c (0.5 mmol), diphenylphosphine oxide 4a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^t$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 134.6 mg (83%) of 5b as white solid, m.p. 112-114 °C.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.86-7.83 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 4H), 7.32 (d, $J$ = 7.8 Hz, 2H), 7.00 (d, $J$ = 7.8 Hz, 2H), 2.25 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 139.2 (d, $J$ = 2.4 Hz), 135.4 (d, $J$ = 3.7 Hz), 132.7 (d, $J$ = 105.9 Hz), 132.3 (d, $J$ = 3.0 Hz), 131.7 (d, $J$ = 10.1 Hz), 130.0 (d, $J$ = 1.8 Hz), 128.6 (d, $J$ = 13.0 Hz), 122.3 (d, $J$ = 5.1 Hz), 21.2. $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 41.2.

HR-MS (ESI): $m/z$ calculated for C$_{19}$H$_{17}$OPS [M+Na]$^+$: 347.0635, found: 347.0634.

S-(4-methoxyphenyl) diphenylphosphinothioate (5c)$^{12}$

Prepared according to general procedure, the reaction of 4-methoxybenzenethiol 1d (0.5 mmol), diphenylphosphine oxide 4a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^t$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 136.1 mg (80%) of 5c as white solid, m.p. 150-152°C.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.86-7.81 (m, 4H), 7.53-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.34-7.31 (m, 2H), 6.74-6.71 (m, 2H), 3.73 (s, 3H).

$^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 160.5 (d, $J$ = 2.3 Hz), 137.1 (d, $J$ = 3.5 Hz), 132.7 (d, $J$ = 105.6 Hz), 132.3 (d, $J$ = 3.0 Hz), 131.7 (d, $J$ = 10.1 Hz), 128.6 (d, $J$ = 13.0 Hz), 116.1 (d, $J$ = 5.0 Hz), 114.8 (d, $J$ = 1.9 Hz), 55.3. $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 41.3.

HR-MS (ESI): $m/z$ calculated for C$_{19}$H$_{17}$O$_2$PS [M+Na]$^+$: 363.0585, found: 363.0599.

S-(4-chlorophenyl) di-p-tolylphosphinothioate (5d)
Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), di-p-tolylphosphine oxide 4b (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 141.6 mg (76%) of 5d as pale yellow solid, m.p. 119-121°C. 

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.71 (dd, $J = 12.7$ Hz, $J = 8.0$ Hz, 4H), 7.38 (dd, $J = 8.4$ Hz, $J = 1.3$ Hz, 2H), 7.25-7.23 (m, 4H), 7.17 (d, $J = 8.5$ Hz, 2H), 2.39 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 143.1 (d, $J = 2.9$ Hz), 136.4 (d, $J = 3.9$ Hz), 135.3 (d, $J = 2.4$ Hz), 131.7 (d, $J = 10.5$ Hz), 129.8 (d, $J = 1.5$ Hz), 129.4 (d, $J = 13.6$ Hz), 128.7 (d, $J = 1.3$ Hz), 125.3 (d, $J = 5.0$ Hz), 21.6. $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 42.0.

HR-MS (ESI): $m/z$ calculated for C$_{20}$H$_{18}$ClOPS [M+Na]$^+$: 395.0402, found: 395.0403.

S-(4-chlorophenyl) bis(4-methoxyphenyl)phosphinothioate (5e)

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), bis(4-methoxyphenyl)phosphine oxide 4c (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 125.5 mg (62%) of 5e as yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta$ 7.77-7.71 (m, 4H), 7.38 (d, $J = 7.2$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 6.95-6.92 (m, 4H), 3.84 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): $\delta$ 162.9 (d, $J = 3.0$ Hz), 136.4 (d, $J = 3.8$ Hz), 135.3 (d, $J = 2.3$ Hz), 133.7 (d, $J = 11.7$ Hz), 129.3 (d, $J = 1.3$ Hz), 125.6 (d, $J = 5.2$ Hz), 123.6 (d, $J = 114.4$ Hz), 114.3 (d, $J = 14.4$ Hz), 55.5 (d, $J = 3.4$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 41.6.

HR-MS (ESI): $m/z$ calculated for C$_{20}$H$_{18}$ClO$_3$PS [M+Na]$^+$: 427.0300, found: 427.0311.

S-(4-fluorophenyl) diphenylphosphinothioate (5f)

Prepared according to general procedure, the reaction of 4-fluorobenzenethiol 1g (0.5 mmol)
mmol), diphenylphosphine oxide 4a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^4$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 88.6 mg (54%) of 5f as white solid, m.p. 93-95°C.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.85-7.81 (m, 4H), 7.53-7.39 (m, 8H), 6.91-6.88 (m, 2H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 163.3 (dd, $J$ = 248.4 Hz, $J$ = 2.3 Hz), 137.3 (dd, $J$ = 8.2 Hz, $J$ = 3.1 Hz), 132.3 (d, $J$ = 2.6 Hz), 132.1 (d, $J$ = 106.2 Hz), 131.5 (d, $J$ = 9.9Hz), 128.5 (d, $J$ = 13.1 Hz), 121.0 (dd, $J$ = 5.2 Hz, $J$ = 3.3 Hz), 116.2 (dd, $J$ = 21.8 Hz, $J$ = 1.7 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 41.7.

HR-MS (ESI): $m/z$ calculated for C$_{18}$H$_{14}$FOPS [M+Na]$^+$: 351.0385, found: 351.0396.

S-(4-aminophenyl) di-p-tolylphosphinothioate (5g)

Prepared according to general procedure, the reaction of 4-aminobenzenethiol 1m (0.5 mmol), di-p-tolylphosphine oxide 4b (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^4$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 155.5 mg (88%) of 5g as yellow oil.

$^1$H NMR (400 MHz, DMSO, ppm): δ 7.68-7.63 (m, 4H), 7.35-7.26 (m, 7H), 6.84 (d, $J$ = 7.9 Hz, 1H), 3.91 (br s, 2H), 2.35 (s, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 147.2 (d, $J$ = 2.2 Hz), 142.6 (d, $J$ = 2.8 Hz), 136.8 (d, $J$ = 3.3 Hz), 131.6 (d, $J$ =10.3 Hz), 130.0 (d, $J$ =1.4 Hz), 129.2 (d, $J$ =13.3 Hz), 116.0 (d, $J$ = 1.8 Hz), 112.6 (d, $J$ = 5.1 Hz), 21.6. $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 42.6.

HR-MS (ESI): $m/z$ calculated for C$_{20}$H$_{20}$NOPS [M+Na]$^+$: 376.4095, found: 376.0906.

S-(naphthalen-2-yl) diphenylphosphinothioate (5h)$^{11}$

Prepared according to general procedure, the reaction of naphthalene-2-thiol 1t (0.5 mmol), diphenylphosphine oxide 4a (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^4$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 160.3 mg (89%) of 5h as white solid, m.p. 108-110°C.

$^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.99 (s, 1H), 7.90-7.86 (m, 4H), 7.75-7.70 (m,
2H), 7.66 (d, J = 8.5 Hz, 1H), 7.51-7.42 (m, 9H). 13C NMR (100 MHz, CDCl3, ppm): δ 135.3 (d, J = 4.8 Hz), 133.4 (d, J = 1.9 Hz), 132.9 (d, J = 1.5 Hz), 132.5 (d, J = 106.3 Hz), 132.2 (d, J= 2.8 Hz), 131.6 (d, J = 10.2 Hz), 131.4 (d, J = 3.1 Hz), 128.6 (d, J = 1.4 Hz), 128.5 (d, J = 13.1 Hz), 127.7, 127.5, 126.7, 126.3, 123.4 (d, J = 5.2 Hz). 31P NMR (162 MHz, CDCl3, ppm): δ 41.5.


S-(2-aminophenyl) bis(4-methoxyphenyl)phosphinothioate (5i)

![5i](image)

Prepared according to general procedure, the reaction of 2-aminobenzenethiol 1r (0.5 mmol), bis(4-methoxyphenyl)phosphine oxide 4c (1.5 mmol), MB (3 mol%) and K2CO3 (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 175.3 mg (91%) of 5i as white solid, m.p. 114-117°C.

1H NMR (400 MHz, CDCl3, ppm): δ 7.78-7.29 (m, 4H), 7.05-7.02 (m, 2H), 6.95-6.92 (m, 4H), 6.68-6.66 (m, 1H), 6.50-6.46 (m, 1H), 3.83 (s, 6H). 13C NMR (100 MHz, CDCl3, ppm): δ 162.8 (d, J = 3.1 Hz), 150.5 (d, J = 2.8 Hz), 137.6 (d, J = 3.2 Hz), 133.5 (d, J = 11.7 Hz), 130.7 (d, J = 2.4 Hz), 124.3 (d, J = 112.2 Hz), 118.5 (d, J = 1.3 Hz), 116.2 (d, J = 2.0 Hz), 114.1 (d, J = 14.1 Hz), 109.4 (d, J = 5.1 Hz), 55.4 (d, J = 3.5 Hz). 31P NMR (162 MHz, CDCl3, ppm): δ 43.8.

HR-MS (ESI): m/z calculated for C20H20NO3PS [M+Na]+: 408.0799, found: 408.0828.

S-(4-fluorophenyl) diisopropylphosphinothioate (5j)

![5j](image)

Prepared according to general procedure, the reaction of 4-fluorobenzenethiol 1g (0.5 mmol), diisopropylphosphine oxide 4d (1.5 mmol), MB (3 mol%) and K2CO3 (0.5 mmol) in i-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.4 mg (71%) of 5j as yellow oil.

1H NMR (400 MHz, CDCl3, ppm): δ 7.61-7.57 (m, 2H), 7.04-7.00 (m, 2H), 2.26-2.17 (m, 2H), 1.28-1.19 (m, 12H). 13C NMR (100 MHz, CDCl3, ppm): δ 163.3 (dd, J = 247.5 Hz, J = 1.7 Hz), 137.4 (dd, J = 8.2 Hz, J = 3.1 Hz), 121.7 (dd, J = 7.8...
Hz, $J = 4.0$ Hz), 116.4 (dd, $J = 21.9$ Hz, $J = 1.3$ Hz), 30.4 (d, $J = 62.6$ Hz), 16.4 (d, $J = 2.9$ Hz), 16.1 (d, $J = 3.1$ Hz). \(^{31}\text{P NMR (162 MHz, CDCl}_3, \text{ppm)}:* \delta 73.4.

**HR-MS (ESI):** $m/z$ calculated for C\(_{12}\)H\(_{18}\)FOPS [M+Na]: 283.0698, found: 283.0696.

**S-(4-chlorophenyl) diisopropylphosphinothioate (5k)**

\[\text{Cl} \quad \text{O} \quad \text{Pr} \quad \text{P} \quad \text{Pr} \]

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), diisopropylphosphine oxide 4d (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \(t\)-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 101.0 mg (73%) of 5k as yellow oil.

**\(^1\text{H NMR (400 MHz, CDCl}_3, \text{ppm)}:** δ 7.56 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 2.27-2.16 (m, 2H), 1.28-1.19 (m, 12H). **\(^{13}\text{C NMR (100 MHz, CDCl}_3, \text{ppm)}:** δ 136.4 (d, $J = 3.1$ Hz), 134.9 (d, $J = 2.0$ Hz), 129.1 (d, $J = 1.3$ Hz), 125.3 (d, $J = 4.7$ Hz), 30.4 (d, $J = 62.7$ Hz), 16.3 (d, $J = 3.0$ Hz), 16.0 (d, $J = 3.2$ Hz). **\(^{31}\text{P NMR (162 MHz, CDCl}_3, \text{ppm)}:** δ 74.5.

**HR-MS (ESI):** $m/z$ calculated for C\(_{12}\)H\(_{18}\)OPS [M+Na]: 299.0402, found: 299.0417.

**S-(4-chlorophenyl) diisopropylphosphinothioate (5l)**

\[\text{Br} \quad \text{O} \quad \text{Pr} \quad \text{Pr} \]

Prepared according to general procedure, the reaction of 4-bromobenzenethiol 1f (0.5 mmol), diisopropylphosphine oxide 4d (1.5 mmol), MB (3 mol%) and K\(_2\)CO\(_3\) (0.5 mmol) in \(t\)-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 117.2 mg (73%) of 5l as colorless oil.

**\(^1\text{H NMR (400 MHz, CDCl}_3, \text{ppm)}:** δ 7.50-7.43 (m, 4H), 2.27-2.16 (m, 2H), 1.28-1.19 (m, 12H). **\(^{13}\text{C NMR (100 MHz, CDCl}_3, \text{ppm)}:** δ 136.9 (d, $J = 3.1$ Hz), 132.3 (d, $J = 1.3$ Hz), 126.1 (d, $J = 4.9$ Hz), 123.3 (d, $J = 1.9$ Hz), 30.6 (d, $J = 62.8$ Hz), 16.5 (d, $J = 2.9$ Hz), 16.2 (d, $J = 3.2$ Hz). **\(^{31}\text{P NMR (162 MHz, CDCl}_3, \text{ppm)}:** δ 73.8.

**HR-MS (ESI):** $m/z$ calculated for C\(_{12}\)H\(_{18}\)BrOPS [M+Na]: 342.9897, found: 342.9899.

**S-(4-chlorophenyl) dicyclohexylphosphinothioate (5m)**
Prepared according to general procedure, the reaction of 4-chlorobenzenethiol 1a (0.5 mmol), dicyclohexylphosphine oxide 4e (1.5 mmol), MB (3 mol%) and K$_2$CO$_3$ (0.5 mmol) in $^t$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 167.7 mg (94%) of 5m as yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.54 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 2.02-1.70 (m, 12H), 1.47-1.39 (m, 4H), 1.25-1.18 (m, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 136.6 (d, J = 3.1 Hz), 135.0 (d, J = 3.1 Hz), 129.3 (d, J = 0.8 Hz), 125.8 (d, J = 4.5 Hz), 40.5 (d, J = 6.8 Hz), 26.6 (d, J = 5.2 Hz) 26.5 (d, J = 5.3 Hz), 26.3 (d, J = 3.3 Hz), 26.0 (d, J = 3.3 Hz), 25.9 (d, J = 1.9 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): δ 67.9.

HR-MS (ESI): m/z calculated for C$_{18}$H$_{26}$ClOPS [M+Na]$^+$: 379.1028, found: 379.1051.

TEMPO adduct

1-(((4-chlorophenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (7)

Colorless oil. $^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.61 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 1.67-1.49 (m, 15H), 0.91 (s, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$, ppm): δ 149.07, 135.80, 128.84, 127.60, 61.61, 59.11, 43.60, 41.49, 35.52, 32.85, 28.86, 28.06, 17.35.

HR-MS (ESI): m/z calculated for C$_{15}$H$_{22}$ClNOS [M+Na]$^+$: 322.1008, found: 322.1010.

2,2,6,6-tetramethylpiperidin-1-yl diphenylphosphinate (8)

White solid, m.p. 115-117°C. $^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 7.87-7.83 (m, 4H), 7.48-7.39 (m, 6H), 1.36-0.94 (m, 18H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ
134.04 (d, $J = 134.2$ Hz), 131.83 (d, $J = 10.0$ Hz), 131.66 (d, $J = 2.7$ Hz), 128.44 (d, $J = 12.7$ Hz), 61.72 (d, $J = 2.7$ Hz), 40.23, 32.62, 17.03. $^{31}$P NMR (162 MHz, CDCl$_3$, ppm): $\delta$ 33.4.

HR-MS (ESI): $m/z$ calculated for C$_{21}$H$_{28}$NO$_2$P [M+Na]$^+$: 380.1750, found: 380.1753.

2.5 The fluorescence emission spectrum of the methylene blue

The fluorescence emission spectrum of the methylene blue showed a peak at 690 nm when excited at 664 nm (Figure S1). The fluorescence emission spectra of methylene blue at different excitation wavelength was tested and the highest emission peak was obtained under the excitation at 664 nm (Figure S2).

![Fluorescence excitation and emission spectra](image1)

**Fig. S1 Fluorescence excitation and emission spectra**

![Fluorescence emission spectra of the methylene blue at different excitation wavelengths](image2)

**Fig. S2 Fluorescence emission spectra of the methylene blue at different excitation wavelengths**

2.6 Determination of quantum yield
The quantum yield of phosphorothioate (3a) formation was determined with a potassium ferrioxalate actinometer. The quantum yield (Φ_P) of this reaction was about 3.5%. This low value is consistent with the long reaction times needed for most substrates.

The process are as follows:
A solution of K₂Fe(C₂O₄)₃ (0.15 M, 2 mL) was transferred into a fused silica cuvette and irradiated for 60 s under blue LEDs (10W). After a illumination period of 60s, 100 μL were transferred to a 10 mL volumetric flask, and 4 mL of a phenanthroline solution (20 mg of 1,10-phenanthroline in 10 mL of H₂O) and 500 μL of a buffer solution (1.8 g of NaOAc and 1 mL of HOAc in H₂O up to 100 mL) were added prior to adding water up to 10 mL.

The moles of Fe²⁺ generated was measured by determining the absorbance of the Fe(II)-o-phenanthroline complex at 510 nm. A blank sample was prepared following the same procedure. Note that the procedure was done under subdued red light illumination conditions.

The moles of Fe²⁺ was calculated according to the follow equation:

\[ mmolFe^{2+} = \frac{A}{s \times n \times \varepsilon} \times \frac{10molL\times2ml}{0.1ml} \]  \hspace{1cm} (1)

A is the absorbance and n is the refractive index. ε is the extinction coefficient of the complex at 510 nm (ε=1.11·10⁴ L·mol⁻¹·cm⁻¹). d is the light path length of the cuvette (d = 1 cm).

The photon flux was calculated using the following formulas:

\[ \text{photon flux} = \frac{mmolFe^{2+}}{10molL\times2ml} \times \frac{10^5mol}{mmol} \]  \hspace{1cm} (2)

Where t is illumination time in 60s, the quantum yield of the photolysis of potassium ferrioxalate (Φ₄₅₀nm = 1) total light absorption (f = 1). Finally, the quantum yield (Φ_P) is given by:

\[ \Phi_P = \frac{mol \, 3a}{t_1 \times \text{photon flux}} \times 100 \]  \hspace{1cm} (3)

Where mol 3a represents the amount of product generated (1.6×10⁻⁵ mol) and t₁ is the reaction time in 18000s.

3 References


$^1$H NMR, $^{13}$C NMR, $^{31}$P NMR of Compounds
3j

140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

3j

14729

.0 9.3 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8 -0.9 -1.0
f2 (ppm)
S80