MULTI-SUBSTITUTED DIBENZOPHOSPHOLE OXIDE SYNTHESIS BY THE CATALYTIC [2+2+2] CYCLOADDITION OF PHOSPHORYL-BENZENE-TETHERED DIYNES WITH VARIOUS ALKYNES

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Dedicated to Prof. Dr. Lutz F. Tietze for the celebration of the 75th birthday

Abstract – Rhodium-catalyzed intermolecular [2+2+2] cycloaddition of phosphorylbenzene-tethered 1,6-diynes with alkynes gave dibenzophosphole oxide derivatives. Various monoalkynes were applicable in this reaction as coupling partners, and dibenzophosphole oxide derivatives substituted with aromatic ring(s) including dibenzothiophene(s) were obtained. The asymmetric desymmetrization of a prochiral phosphorylbenzene-tethered triyne gave a chiral dibenzophosphole oxide derivative with high ee.

INTRODUCTION

Dibenzoheteroles are condensed tricyclic compounds that have a heterole between two benzene rings. Among them, dibenzophosphole (DBP) oxide skeleton has attracted considerable attention as organic molecular devices due to their highly electron-accepting character.¹-³ Polymers,⁴ helical⁵ and ladder-type⁶ compounds containing the DBP oxide have been synthesized, and their physical properties were investigated. Because of wide applicability of DBP oxide derivatives, several synthetic approaches have been developed. For example, radical phosphorylation using (Me₃Sn)₂PPh and 1,1′-azobis(cyclohexane-1-carbonitrile (V-40),³⁶ and radical cyclization with triethylborane and oxygen⁶⁰ were reported. As for catalytic approaches, Pd-catalyzed direct arylation initiated by C-H or/and C-P
bond cleavage and Pd-catalyzed dehydrogenative cyclization were recently disclosed. However, most of these examples are the synthesis of non- or monosubstituted DBP oxides. Therefore, a conventional approach to the synthesis of multi-substituted DBP oxides is strongly desired.

Transition-metal-catalyzed [2+2+2] cycloaddition is a reliable and atom-economical protocol for the construction of condensed polycyclic ring systems. The dibenzoheteroles, such as carbazoles, dibenzofurans, and dibenzosiloles have been prepared by the [2+2+2] cycloaddition of alkynes. Tanaka et al. developed Rh-catalyzed [2+2+2] cycloaddition of dialkynyl phosphorus and tetrynes for the synthesis of helical compounds containing DBP skeleton. We have comprehensively studied [2+2+2] cycloaddition of various substrates with alkyne motifs, and we recently reported the synthesis of dibenzothiophene (DBT) and dibenzothiophene dioxide derivatives using [2+2+2] cycloaddition of sulfanylbenzene-tethered 1,6-diynes with alkynes. We further considered that the reaction of phosphorylbenzene-tethered 1,6-diynes with alkynes could be a new approach to the synthesis of multi-substituted DBP oxide derivatives.

RESULTS AND DISCUSSION

According to our previous results, we examined the reaction of phosphorylbenzene-tethered 1,6-diyne 1a with dimethyl acetylenedicarboxylate (DMAD) (2a) in the presence of a cationic rhodium catalyst using BIPHEP (2,2’-bis(diphenylphosphino)-1,1’-biphenyl) as a diphosphine ligand at 80 °C. Table 1 shows the effect of the counter anion of cationic rhodium complex: in each entry, diyne 1a was completely consumed within 1 h, and the desired multi-substituted DBP oxide 3aa was obtained. Tetrafluoroborate (BF₄) and hexafluorophosphate (PF₆) gave the comparable good yields (Entries 1 and 2). Trifluoromethanesulfonate (OTf) and hexafluoroantimonate (SbF₆) gave poor results, because the significant amounts of dimer of 1a were formed by self-cycloaddition (Entries 3 and 4). In contrast, tetrakis(3,5-bistrifluoromethylphenyl)borate (BARF) gave the best yield of 85% by almost complete suppression of self-cycloaddition (Entry 5).

Table 1. Effect of counter anion on the [2+2+2] cycloaddition of diyne 1a with 2a
Under the reaction conditions of entry 5 in Table 1, various phosphorylbenzene-tethered diynes were subjected to the intermolecular [2+2+2] cycloaddition (Table 2). The reaction of diyne 1b, which has phenyl and pentyl groups on its alkyne termini of \( R_1 \) and \( R_2 \) respectively, scarcely proceeded (Entry 1). The reaction of diyne 1c with two phenyl groups proceeded, but the yield of the desired cycloadduct 3ca was low (Entry 2). Diynes 1b and 1c were inappropriate substrates due to the formation of self-cycloadducts prior to cross-cycloadducts. The introduction of an alkyl group as \( R_1 \) was critical for high yield: the reaction of diyne 1d, which has pentyl and 4-methylphenyl groups, effectively proceeded to give desired cycloadduct 3da in 86% yield (Entry 3). The cycloaddition of diynes 1e and 1f, which have methoxyphenyl and chlorophenyl group, respectively as \( R_1 \), also proceeded to give the corresponding products 3ea and 3fa in high yields (Entries 4 and 5). Diyne 1g possessing a biphenyl group was also a good substrate, and the desired cycloadduct 3ga was obtained in 86% yield (Entry 6). In addition, as shown in the reaction of diyne 1h, thiophene could also be successfully installed into the target product in excellent yield (Entry 7).

### Table 2. [2+2+2] Cycloaddition of various diynes 1 with 2a

<table>
<thead>
<tr>
<th>Entry a</th>
<th>Diyne</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b</td>
<td>Ph</td>
<td>( n)-C(<em>5)H(</em>{11})</td>
<td>trace (3ba)</td>
</tr>
<tr>
<td>2</td>
<td>1c</td>
<td>Ph</td>
<td>Ph</td>
<td>27 (3ca)</td>
</tr>
<tr>
<td>3</td>
<td>1d</td>
<td>( n)-C(<em>5)H(</em>{11})</td>
<td>C(_6)H(_4)(p-Me)</td>
<td>86 (3da)</td>
</tr>
<tr>
<td>4</td>
<td>1e</td>
<td>( n)-C(<em>5)H(</em>{11})</td>
<td>C(_6)H(_4)(p-OMe)</td>
<td>84 (3ea)</td>
</tr>
<tr>
<td>5</td>
<td>1f</td>
<td>( n)-C(<em>5)H(</em>{11})</td>
<td>C(_6)H(_4)(p-Cl)</td>
<td>80 (3fa)</td>
</tr>
</tbody>
</table>
Diyne/alkyne was 1/3. Diyne was added dropwise to a solution of the Rh catalyst and alkyne 2a.

Next, we examined the reaction of diyne 1a with various symmetrical alkynes (Table 3). 2-Butyne-1,4-diol (2b) could be used, and the corresponding diol 3ab was obtained in high yield (Entry 1). Dialkyl-substituted alkyne 2c could be also used as a coupling partner, and the desired cycloadduct 3ac was obtained in 93% yield (Entry 2). It is noteworthy that the reaction using diphenylacetylene (2d) also proceeded to afford polyarylated DBP oxide derivative 3ad in good yield (Entry 3). The cycloaddition using other diarylacetylenes 2e and 2f, which have electron-donating and -withdrawing groups, respectively gave the corresponding products 3ae and 3af (Entries 4 and 5). The reaction of boryl-substituted diarylacetylene 2g could also be achieved, and the obtained DBP oxide derivative 3ag can be used for further transformation (Entry 6). In addition, 1,2-di(thiophen-2-yl)ethyne (2h) was also a good coupling partner, and the desired cycloadduct 3ah containing two thiophenyl groups was obtained in 90% yield (Entry 7).

Table 3. Cycloaddition of diyne 1a with various symmetrical alkynes 2

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne</th>
<th>R³</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2b</td>
<td>CH₂OH</td>
<td>91 (3ab)</td>
</tr>
<tr>
<td>2</td>
<td>2c</td>
<td>n-C₅H₁₁</td>
<td>93 (3ac)</td>
</tr>
<tr>
<td>3</td>
<td>2d</td>
<td>Ph</td>
<td>81 (3ad)</td>
</tr>
<tr>
<td>4</td>
<td>2e</td>
<td>C₆H₄(p-OMe)</td>
<td>77 (3ae)</td>
</tr>
<tr>
<td>5</td>
<td>2f</td>
<td>C₆H₄(p-Br)</td>
<td>57 (3af)</td>
</tr>
<tr>
<td>6</td>
<td>2g</td>
<td>C₆H₄(p-Bpin)</td>
<td>58 (3ag)</td>
</tr>
<tr>
<td>7</td>
<td>2h</td>
<td>2-thienyl</td>
<td>90 (3ah)</td>
</tr>
</tbody>
</table>

*Diyne/alkyne was 1/3. Diyne 1a was added dropwise to a solution of the Rh catalyst and alkyne.*

The cycloaddition using unsymmetrical alkynes also proceeded under the same reaction conditions (Scheme 1). The reaction of 1a with ethyl phenylpropionate (2i) gave the desired products in 92% total yield as a mixture of 3ai and 4ai without regioselectivity. In the case of ethynylbenzene (2j), almost quantitative yield was achieved, and cycloadduct 3aj was the major product.
Scheme 1. Cycloaddition of diyne 1a with unsymmetrical alkynes 2i and 2j

As sulfur analogue of phosphoryl benzene-tethered diyne 1a, we next examined the cycloaddition with diyne 5 for the synthesis of dibenzothiophene 5-oxide derivatives under the same reaction conditions (Scheme 2). The reaction using DMAD (2a) smoothly proceeded, and the desired cycloadduct 6a was obtained in 69% yield. Diphenylacetylene (2d) could be also used to form multi-aryl substituted DBT 5-oxide 6d in high yield.

Scheme 2. Synthesis of dibenzothiophene 5-oxide derivatives

The asymmetric desymmetrization using [2+2+2] cycloaddition has already been reported: the reaction of symmetrical dialkynyl alcohol\(^\text{15}\) or dialkynylphosphine oxide\(^\text{16}\) with diynes gave chiral cycloadducts. Recently, the [2+2+2] cycloaddition of prochiral silicon-tethered triyne with monoalkyne has been developed for the enantioselective synthesis of chiral dibenzosiloles.\(^\text{17}\) Against this background, we next focused on the asymmetric desymmetrization using phosphoryl benzene-tethered triyne (Scheme 3). We examined the [2+2+2] cycloaddition of prochiral triyne 7 with 2-butyne-1,4-diol (2b) using Rh -(S)-BINAP catalyst. The reaction smoothly proceeded to give the desired chiral DBP oxide 8 in high yield with good ee. Chiral DBP oxides have been prepared by optical resolution,\(^\text{18}\) but this is the first example of enantioselective protocol, as far as we know.
Scheme 3. Enantioselective desymmetrization of 7 by the [2+2+2] cycloaddition

In the light of the application of DBP oxide derivatives, we synthesized the DBP oxides possessing dibenzothiophene(s) (DBT) as substituent(s) (Schemes 4 and 5). The reaction of diyne 1i, which has dibenzo[b,d]thiophen-2-yl group on one of its alkyne termini, proceeded to give the desired DBP oxide 3ia in 80% yield. Diphenylacetylene (2d) could also be used, and the polyarylated DBP oxide derivative 3id was afforded in high yield. We further examined the cycloaddition of dibenzothiophene-containing alkyne (2k) with diyne 1a, which gave DBP oxide derivative 3ak as a major regioisomer.

Scheme 4. Synthesis of bi-dibenzo-heteroles

In addition, we examined the cycloaddition using alkyne 2l, which has dibenzothiophene moieties on both of its termini (Scheme 5). The desired cycloadduct 3al consisting of a DBP oxide and two DBTs was obtained in moderate yield, although both alkyne 2l and cycloadduct 3al were hardly dissolved even in
1,2-dichloroethane. When dialkylated alkyne 2m was used, the solubility of the alkyne and the cycloadduct was surely increased but the yield was not improved.

Scheme 5. Synthesis of ter(dibenzoheterolyl)s

We measured the UV-vis spectra of the obtained DBP oxide derivatives 3ad, 3id, 3ak and 3al to investigate the effect of DBT substituent(s) on the physical properties (Table 5). The $\lambda_{\text{max}}$ of these compounds were observed at 317.6-338.0 nm. There is no significant difference in the value of $\lambda_{\text{max}}$ among 3ad, 3id and 3al. In the case of DBT substituent(s) derivatives, obvious red-shift of disubstituted 3al was observed compared with monosubstituted 3ak (Entry 3 vs Entry 4).

Table 5. UV-vis date of 3ad, 3id, 3ak, 3al

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>UV-vis $\lambda_{\text{max}}$ (nm) / log $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3ad</td>
<td>338.0 / 3.45</td>
</tr>
<tr>
<td>2</td>
<td>3id</td>
<td>332.0 / 3.21</td>
</tr>
<tr>
<td>3</td>
<td>3ak</td>
<td>317.6 / 3.65</td>
</tr>
<tr>
<td>4</td>
<td>3al</td>
<td>332.2 / 3.09</td>
</tr>
</tbody>
</table>

Finally, we examined the synthetic transformation of cycloadduct 3ac by using Lawesson’s reagent and obtained dibenzophosphole sulfide 9 in excellent yield (Scheme 6).

Scheme 6. Synthesis of dibenzophosphole sulfide derivative
In conclusion, we developed Rh-catalyzed [2+2+2] cycloaddition of phosphorylbenzene-tethered and sulfinylbenzene-tethered 1,6-diynes with alkynes for the synthesis of DBP and DBT oxide derivatives. The present reaction provides a new and powerful protocol for the synthesis of multi-substituted DBP oxide derivatives, and the DBP oxide derivatives possessing one or two DBT moieties were also obtained. In addition, we achieved the first and highly enantioselective synthesis of a chiral DBP oxide. We will further synthesize various DBP oxides including chiral ones and containing other benzoheterole(s), and evaluate them as electronic materials.

**EXPERIMENTAL**

**General.** All reactions were examined under an argon atmosphere in oven-dried glassware with a magnetic stirring bar. Dehydrated 1,2-dichloroethane were purchased from Wako Pure Chemical Industries Ltd. (Wako) and degassed by argon bubbling before use. Other reagents were purchased from Wako, Kanto, TCI, or Aldrich and were used without further purification. Flash column chromatography was performed with silica gel (Kanto Chemical Co., Inc. 60 N). Preparative thin-layer chromatography (PTLC) was performed with silica gel precoated glass plates (Merck 60 GF254) prepared in our laboratory. FT-IR spectra were recorded with Horiba FT/IR-4200 spectrophotometer. NMR spectra were measured with JEOL ECX500 (1H NMR, 495.13 MHz; 13C NMR, 124.5 MHz; 31P NMR, 200.43 MHz) using TMS as an internal standard, CDCl3 and DMSO-d6 were used as solvents. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-SX102A with FAB (Fast Atomic Bombardment) method or JMS-T100CS with ESI (Electro Spray Ionization) method.

**Hept-1-yn-1-yl(phenyl)(2-(phenylethynyl)phenyl)phosphine oxide (1a):** a pale yellow oil; IR (CH2Cl2) 2924, 1438, 758, 691 cm-1; 1H NMR δ 0.80 (t, J = 7.3 Hz, 3H), 1.17-1.30 (m, 4H), 1.45-1.50 (m, 2H), 2.34 (dt, Jd = 3.6 Hz, Jt = 7.2 Hz, 2H), 7.22-7.61 (m, 11H), 7.81-7.85 (m, 2H), 8.26-8.31 (m, 1H); 13C NMR δ 13.9, 19.9, 22.1, 27.3, 31.1, 73.8, 75.2, 87.7, 97.5, 109.5, 122.8, 125.6, 125.6, 128.0, 128.1, 128.3, 128.4, 128.7, 131.0, 131.1, 131.4, 131.9, 131.9, 132.0, 132.0, 132.7, 133.1, 133.4, 133.6, 133.7, 134.1; 31P NMR δ 5.9; HRMS (ESI positive) m/z calcld for C27H25NaOP ([M+Na]+): 419.1535. Found: 419.1527.

**Phenyl(phenylethynyl)(2-(phenylethynyl)phenyl)phosphine oxide (1b):** a yellow oil; IR (CH2Cl2) 2924, 1438, 758, 691 cm-1; 1H NMR δ 0.80-0.82 (m, 3H), 1.17-1.18 (m, 4H), 1.28-1.30 (m, 2H), 2.12 (t, J = 7.2 Hz, 2H), 7.35-7.60 (m, 11H), 7.84-7.88 (m, 2H), 8.26-8.31 (m, 1H); 13C NMR δ 13.8, 19.6, 22.1, 27.7, 31.1, 78.7, 82.0, 83.4, 100.0, 104.3, 104.5, 120.4, 120.4, 126.5, 126.6, 127.3, 127.4, 128.2, 128.3, 128.5, 130.4, 130.8, 130.9, 131.8, 131.9, 132.1, 132.5, 132.9, 133.2, 133.2, 133.6, 133.7, 133.9; 31P NMR δ 7.3; HRMS (ESI positive) m/z calcld for C27H25NaOP ([M+Na]+): 419.1535. Found: 419.1533.

**Phenyl(phenylethynyl)(2-(phenylethynyl)phenyl)phosphine oxide (1c):** a pale yellow oil; IR (CH2Cl2)
$2922, 2359, 1739, 1202, 690, 407 \text{ cm}^{-1}$; $^1\text{H NMR } \delta 7.04-7.17 (m, 4H), 7.20-7.45 (m, 13H), 7.75-7.78 (m, 1H), 7.82-7.85 (m, 1H); $^{13}\text{C NMR } \delta 81.9, 83.3, 87.6, 87.7, 88.9, 88.9, 97.2, 97.8, 120.2, 120.2, 122.3, 122.6, 122.7, 125.6, 125.7, 127.6, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.7, 128.7, 129.1, 129.2, 129.2, 130.4, 131.0, 131.0, 131.1, 131.4, 131.5, 131.9, 132.1, 132.2, 132.2, 132.6, 133.2, 133.3, 133.4, 133.4, 133.5, 133.6, 133.7, 133.7, 133.8, 133.8, 134.2, 134.6, 136.3; $^{31}\text{P NMR } \delta 6.7; \text{HRMS (ESI positive) } m/z \text{ calcd for } C_{28}H_{19}NaOP ([M+Na]^+): 425.1066. \text{Found: } 425.1064.

**Hept-1-yn-1-yl(phenyl)(2-(4-tolylethynyl)phenyl)phosphine oxide (1d)**: a pale yellow oil; IR (CH$_2$Cl$_2$) 2924, 2852, 2194, 1465, 1200, 538 \text{ cm}^{-1}; $^1\text{H NMR } \delta 0.81 (t, J = 7.1 \text{ Hz}, 3H), 1.16-1.31 (m, 4H), 1.45-1.51 (m, 2H), 2.32-2.35 (m, 5H), 7.08-7.13 (m, 4H), 7.37-7.41 (m, 4H), 7.46-7.60 (m, 2H), 7.81-7.85 (m, 2H), 8.26-8.30 (m, 1H); $^{13}\text{C NMR } \delta 13.9, 14.2, 19.9, 19.9, 21.6, 22.1, 27.3, 27.3, 29.8, 31.1, 68.1, 73.2, 80.3, 97.9, 119.8, 125.8, 127.0, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 128.8, 129.0, 129.8, 130.6, 131.0, 131.1, 131.3, 131.9, 132.0, 132.0, 133.3, 133.4, 133.6, 133.6, 134.1, 135.5, 138.9; $^{31}\text{P NMR } \delta 5.9; \text{HRMS (ESI positive) } m/z \text{ calcd for } C_{28}H_{27}NaOP ([M+Na]^+): 433.1692. \text{Found: } 433.1692.

**Hept-1-yn-1-yl(2-(4-methoxyphenylethynyl)phenyl)(phenyl)phosphine oxide (1e)**: a pale yellow oil; IR (CH$_2$Cl$_2$) 2927, 2193, 1605, 1511, 1251, 1200 \text{ cm}^{-1}; $^1\text{H NMR } \delta 0.81 (t, J = 7.2 \text{ Hz}, 3H), 1.19-1.50 (m, 6H), 2.33 (dt, J_d = 3.5 \text{ Hz}, J_t = 7.2 \text{ Hz}, 2H), 3.81 (s, 3H), 6.80-6.82 (m, 2H), 7.15-7.18 (m, 2H), 7.38-7.58 (m, 6H), 7.80-7.85 (m, 2H), 8.24-8.29 (m, 1H); $^{13}\text{C NMR } \delta 13.9, 19.9, 19.9, 22.1, 27.3, 27.3, 31.1, 55.4, 55.4, 55.4, 55.4, 73.8, 75.3, 86.6, 86.6, 97.8, 109.1, 109.3, 113.9, 114.0, 115.0, 126.0, 126.0, 127.7, 127.8, 128.3, 128.4, 131.0, 131.1, 131.9, 132.0, 132.0, 133.2, 133.2, 133.3, 133.3, 133.4, 133.5, 134.2, 160.0; $^{31}\text{P NMR } \delta 6.1; \text{HRMS (ESI positive) } m/z \text{ calcd for } C_{28}H_{27}NaOP ([M+Na]^+): 449.1641. \text{Found: } 449.1641.

**2-(4-Chlorophenylethynyl)phenyl(hept-1-yn-1-yl)(phenyl)phosphine oxide (1f)**: a yellow oil; IR (CH$_2$Cl$_2$) 2928, 2193, 1583, 1491, 1201, 693, 535 \text{ cm}^{-1}; $^1\text{H NMR } \delta 0.82 (t, J = 7.1 \text{ Hz}, 3H), 1.17-1.32 (m, 4H), 1.46-1.52 (m, 2H), 2.34 (dt, J_d = 3.5 \text{ Hz}, J_t = 6.9 \text{ Hz}, 2H), 7.13-7.16 (m, 2H), 7.25-7.27 (m, 2H), 7.38-7.42 (m, 2H), 7.47-7.61 (m, 4H), 7.78-7.83 (m, 2H), 8.22-8.27 (m, 1H); $^{13}\text{C NMR } \delta 13.8, 19.8, 19.8, 22.0, 27.2, 30.9, 73.7, 88.5, 88.5, 96.2, 109.2, 109.5, 121.2, 125.1, 125.2, 128.1, 128.2, 128.3, 128.5, 130.9, 131.0, 131.9, 132.0, 132.0, 132.5, 132.7, 132.9, 133.3, 133.4, 133.5, 133.5, 133.7, 133.9, 134.7; $^{31}\text{P NMR } \delta 6.0; \text{HRMS (ESI positive) } m/z \text{ calcd for } C_{27}H_{23}ClNaOP ([M+Na]^+): 453.1146. \text{Found: } 453.1139.

**Hept-1-yn-1-yl(phenyl)(2-(4-phenylphenylethynyl)phenyl)phosphine oxide (1g)**: a pale yellow oil; IR (CH$_2$Cl$_2$) 2928, 2193, 1488, 1200, 764, 697, 529 \text{ cm}^{-1}; $^1\text{H NMR } \delta 0.79 (t, J = 7.4 \text{ Hz}, 3H), 1.15-1.32 (m, 4H), 1.47-1.53 (m, 2H), 2.36 (dt, J_d = 3.7 \text{ Hz}, J_t = 7.2 \text{ Hz}, 2H), 7.29-7.30 (m, 2H), 7.36-7.63 (m, 13H), 7.83-7.88 (m, 2H), 8.26-8.31 (m, 1H); $^{13}\text{C NMR } \delta 13.8, 19.8, 19.9, 22.0, 27.3, 31.0, 73.8, 75.2, 88.4, 97.4, 109.2, 109.4, 121.6, 126.9, 127.0, 127.8, 128.0, 128.1, 128.3, 128.4, 128.9, 131.0, 131.1, 131.8, 131.9,
131.9, 132.0, 132.6, 133.1, 133.3, 133.4, 133.6, 133.6, 133.6, 133.6, 140.2, 141.4; \(^{31}\)P NMR δ 6.0; HRMS (ESI positive) \(m/z\) calc for C\(_{33}\)H\(_{29}\)NaOP ([M+Na\(^+\)]): 495.1848. Found: 495.1852.

**Hept-1-yn-1-yl(phenyl)(2-(thiophen-2-ylethynyl)phenyl)phosphine oxide (1h):** a pale yellow oil; IR (CH\(_2\)Cl\(_2\)) 2923, 2360, 2192, 1738, 1200, 694, 526 cm\(^{-1}\); \(^1\)H NMR δ 0.82 (t, \(J = 6.9\) Hz, 3H), 1.19-1.26 (m, 2H), 1.28-1.34 (m, 2H), 1.48-1.56 (m, 2H), 2.38 (dt, \(J_d = 3.5\) Hz, \(J_t = 7.2\) Hz, 2H), 6.96-6.98 (m, 1H), 7.05-7.06 (m, 1H), 7.29-7.30 (m, 1H), 7.39-7.58 (m, 6H), 7.82-7.87 (m, 2H), 8.29-8.34 (m, 1H); \(^{13}\)C NMR δ 13.8, 19.9, 19.9, 22.0, 27.2, 31.0, 73.4, 74.8, 90.9, 91.2, 91.3, 109.4, 109.7, 122.7, 125.0, 125.1, 127.1, 127.3, 127.9, 128.1, 128.2, 128.3, 128.4, 128.4, 128.6, 130.9, 131.0, 131.0, 131.1, 131.9, 131.9, 132.1, 132.1, 132.2, 132.6, 132.7, 132.9, 133.2, 133.3, 133.4, 133.6, 133.9; \(^{31}\)P NMR δ 5.6; HRMS (ESI positive) \(m/z\) calc for C\(_{25}\)H\(_{23}\)NaOPS ([M+Na\(^+\)]): 425.1099. Found: 425.1098.

(2-(Dibenzo[\(b,d\)]thiophen-2-ylethynyl)phenyl)(hept-1-yn-1-yl)phenylphosphine oxide (1i): a pale yellow oil; IR (CH\(_2\)Cl\(_2\)) 2925, 2193, 1474, 1200, 764, 529 cm\(^{-1}\); \(^1\)H NMR δ 0.71 (t, \(J = 7.3\) Hz, 3H), 1.07-1.14 (m, 2H), 1.20-1.26 (m, 2H), 1.43-1.49 (m, 2H), 2.31-2.35 (m, 2H), 7.31 (dd, \(J = 1.5, 8.3\) Hz, 1H), 7.42-7.46 (m, 2H), 7.48-7.61 (m, 5H), 7.64-7.67 (m, 1H), 7.76 (d, \(J = 8.7\) Hz, 1H), 7.84-7.90 (m, 3H), 7.94 (d, \(J = 1.0\) Hz, 1H), 8.09-8.13 (m, 1H), 8.28-8.33 (m, 1H); \(^{13}\)C NMR δ 13.8, 19.9, 19.9, 22.0, 27.3, 27.4, 31.0, 73.9, 75.4, 87.7, 87.8, 97.8, 109.3, 109.5, 118.9, 121.7, 122.7, 123.0, 124.7, 124.8, 125.6, 125.7, 127.3, 128.1, 128.2, 128.4, 128.5, 129.4, 131.1, 131.1, 131.2, 132.0, 132.1, 132.1, 132.6, 133.3, 133.5, 133.5, 133.6, 133.6, 134.3, 134.9, 135.6, 139.8, 140.0; \(^{31}\)P NMR δ 6.0; HRMS (ESI positive) \(m/z\) calc for C\(_{33}\)H\(_{29}\)NaOPS ([M+Na\(^+\)]): 525.1412. Found: 525.1414.

(Hept-1-yn-1-yl)(2-(phenylethynyl)phenyl) sulfoxide (5): Sulfoxide 5 was prepared by the oxidation of the corresponding sulfide using mCPBA: a pale yellow oil; IR (CH\(_2\)Cl\(_2\)) 2955, 2350, 2312, 1492, 1463, 1081 cm\(^{-1}\); \(^1\)H NMR δ 0.78 (t, \(J = 7.3\) Hz, 3H), 1.15-1.29 (m, 4H), 1.44-1.50 (m, 2H), 2.34 (dt, \(J_d = 2.6\) Hz, \(J_t = 7.2\) Hz, 2H), 7.37-7.40 (m, 3H), 7.50 (ddd, \(J = 1.2, 7.5, 7.5\) Hz, 1H), 7.55-7.61 (m, 4H), 8.05 (dd, \(J = 1.6, 7.9\) Hz, 1H); \(^{13}\)C NMR δ 13.8, 19.8, 22.1, 27.3, 30.9, 77.7, 84.3, 98.6, 104.8, 120.4, 122.5, 124.1, 128.6, 129.2, 129.4, 130.9, 131.7, 132.6, 145.5; HRMS (ESI positive) \(m/z\) calc for C\(_{23}\)H\(_{20}\)NaOS ([M+Na\(^+\)]): 343.1127. Found: 343.1126.

**Hept-1-yn-1-yl-bis(2-(4-tolylenethynyl)phenyl)phosphine oxide (7):** a yellow solid; mp 127 °C; IR (CH\(_2\)Cl\(_2\)) 2954, 2925, 2193, 1510, 1202, 817 cm\(^{-1}\); \(^1\)H NMR δ 0.77 (t, \(J = 7.0\) Hz, 3H), 1.10-1.28 (m, 4H), 1.40-1.48 (m, 2H), 2.31 (dt, \(J_d = 3.6\) Hz, \(J_t = 7.0\) Hz, 2H), 2.35 (s, 6H), 7.08 (d, \(J = 8.1\) Hz, 4H), 7.15 (d, \(J = 8.1\) Hz, 4H), 7.28-7.32 (m, 2H), 7.41-7.45 (m, 2H), 7.53-7.56 (m, 2H), 8.23-8.28 (m, 2H); \(^{13}\)C NMR δ 13.8, 19.9, 20.0, 21.6, 22.1, 27.3, 27.3, 31.1, 74.1, 75.6, 87.0, 87.0, 97.2, 108.7, 109.0, 119.9, 125.3, 125.4, 127.5, 127.6, 128.9, 131.5, 131.5, 131.6, 133.2, 133.5, 133.6, 133.8, 133.9, 134.2, 138.7; \(^{31}\)P NMR δ 4.9; HRMS (ESI positive) \(m/z\) calc for C\(_{37}\)H\(_{33}\)NaOP ([M+Na\(^+\)]): 547.2161. Found: 547.2162.

**Typical procedure for the Rh-catalyzed cycloaddition:** [Rh(cod)\(_2\)]BARF (5.9 mg, 0.005 mmol) and
BIPHEP (2.6 mg, 0.005 mmol) were placed in a Schlenk tube, which was then evacuated and backfilled with argon three times. 1,2-Dichloroethane (0.15 mL) and an alkyne (21.3 mg, 0.15 mmol) was added, and the mixture was stirred at 80 °C. Then, a 1,2-dichloroethane solution (1.85 mL) of diyne (0.05 mmol) was added dropwise for 1 h. Solvent was excluded from the reaction mixture under reduced pressure, and the obtained crude products were purified by PTLC to give a pure cycloaduct.

**Dimethyl 4-pentyl-1,5-diphenyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3aa):** a pale yellow solid; mp 68 °C; IR (CHCl₃) 2925, 1737, 1437, 1216, 1206, 704, 550 cm⁻¹; ¹H NMR δ 0.76-0.90 (m, 4H), 1.07-1.22 (m, 4H), 1.44-1.52 (m, 1H), 2.93-3.06 (m, 2H), 3.46 (s, 3H), 3.83 (s, 3H), 6.38-6.40 (m, 1H), 7.12-7.15 (m, 1H), 7.24-7.28 (m, 1H), 7.30-7.32 (m, 1H), 7.37-7.40 (m, 1H), 7.41-7.44 (m, 2H), 7.50-7.54 (m, 4H), 7.60-7.69 (m, 3H); ¹³C NMR δ 5.0, 13.8, 22.2, 31.0, 32.1, 50.5, 52.2, 52.6, 52.6, 125.8, 128.7, 128.8, 128.9, 129.1, 129.2, 129.4, 129.6, 129.6, 129.7, 129.9, 130.7, 131.2, 131.3, 132.3, 132.3, 133.0, 133.1, 133.9, 134.6, 134.8, 136.1, 137.1, 140.0, 140.5, 140.7, 145.6, 167.4, 167.8; ³¹P NMR δ 31.8; HRMS (ESI positive) m/z calcd for C₃₃H₃₃NaO₅ [(M+Na)⁺]: 561.1801. Found: 561.1801.

**Dimethyl 1,4,5-triphenyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3ca):** a white solid; mp 223 °C; IR (CHCl₃) 2920, 2365, 1740, 1238, 700, 528 cm⁻¹; ¹H NMR δ 3.41 (s, 3H), 3.49 (s, 3H), 4.63-4.66 (m, 2H), 6.92-6.95 (m, 1H), 7.00-7.04 (m, 2H), 7.13-7.18 (m, 3H), 7.26-7.38 (m, 4H), 7.44-7.47 (m, 1H), 7.53-7.61 (m, 5H), 7.81-7.83 (m, 1H); ¹³C NMR δ 52.3, 52.4, 66.2, 115.0, 116.1, 116.4, 119.0, 121.5, 126.0, 127.1, 127.3, 127.8, 127.9, 127.9, 128.0, 128.1, 128.2, 128.2, 128.8, 128.8, 128.9, 129.0, 129.3, 129.6, 129.7, 129.8, 130.8, 130.9, 131.1, 131.2, 131.8, 131.9, 132.4, 133.0, 134.6, 135.7, 137.0, 137.7, 154.4, 160.2; ³¹P NMR δ 31.3; HRMS (ESI positive) m/z calcd for C₃₄H₂₅NaO₅ [(M+Na)⁺]: 567.1322. Found: 567.1329.

**Dimethyl 4-pentyl-5-phenyl-1-(4-tolyl)-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3da):** a pale brown solid; mp 63 °C; IR (CHCl₃) 2925, 1736, 1437, 1244, 1207, 731 cm⁻¹; ¹H NMR δ 0.77 (t, J = 7.0 Hz, 3H), 0.81-0.89 (m, 1H), 1.08-1.21 (m, 4H), 1.42-1.51 (m, 1H), 2.48 (s, 3H), 2.93-3.05 (m, 2H), 3.49 (s, 3H), 3.83 (s, 3H), 6.46-6.48 (m, 1H), 7.14-7.18 (m, 2H), 7.25-7.31 (m, 4H), 7.40-7.44 (m, 2H), 7.51-7.54 (m, 1H), 7.60-7.68 (m, 3H); ¹³C NMR δ 13.8, 21.5, 22.2, 31.0, 32.1, 32.2, 32.3, 40.2, 52.2, 52.6, 125.8, 125.9, 127.0, 128.7, 128.8, 129.0, 129.2, 129.5, 129.5, 129.6, 129.8, 130.0, 131.0, 131.2, 131.3, 132.3, 133.0, 133.9, 134.9, 134.7, 134.7, 138.4, 140.2, 140.2, 140.8, 141.8, 142.0, 143.0, 145.3, 145.4, 167.4, 167.8; ³¹P NMR δ 31.7; HRMS (ESI positive) m/z calcd for C₃₄H₂₅NaO₅ [(M+Na)⁺]: 575.1958. Found: 575.1956.

**Dimethyl 1-(4-methoxyphenyl)-4-pentyl-5-phenyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3ea):** a white solid; mp 102 °C; IR (CHCl₃) 2925, 1736, 1610, 1247, 1205, 733 cm⁻¹; ¹H NMR δ 0.77 (t, J = 7.0 Hz, 3H), 0.83-0.89 (m, 1H), 1.08-1.22 (m, 4H), 1.43-1.50 (m, 1H), 2.93-3.05 (m, 2H), 3.51 (s, 3H), 3.83 (s, 3H), 3.92 (s, 3H), 6.51 (dd, J = 3.1, 8.2 Hz, 1H), 7.02-7.05 (m, 2H), 7.16-7.22 (m,
2H), 7.25-7.30 (m, 2H), 7.40-7.44 (m, 2H), 7.51-7.54 (m, 1H), 7.60-7.68 (m, 3H); $^{13}$C NMR δ 13.9, 22.2, 31.1, 32.1, 32.3, 52.3, 52.6, 52.6, 55.3, 114.3, 114.5, 125.8, 125.9, 128.8, 128.8, 128.9, 129.1, 129.6, 129.6, 129.7, 129.7, 130.5, 130.6, 130.8, 131.0, 131.3, 131.3, 132.3, 132.4, 133.1, 133.1, 134.7, 134.9, 142.2, 142.3, 144.5, 145.4, 159.8, 168.0; $^{31}$P NMR δ 31.8; HRMS (ESI positive) m/z calc for C$_{34}$H$_{33}$NaO$_8$P ([M+Na$^+$]): 591.1907. Found: 591.1904.

**Dimethyl 1-(4-chlorophenyl)-4-pentyl-5-phenyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3fa):** a pale yellow solid; mp 151 °C; IR (CH$_2$Cl$_2$) 2955, 1734, 1444, 1229, 986, 737 cm$^{-1}$; $^1$H NMR δ 0.78 (t, $J = 6.9$ Hz, 3H), 0.81-0.88 (m, 1H), 1.08-1.22 (m, 4H), 1.43-1.49 (m, 1H), 2.93-3.05 (m, 2H), 3.51 (s, 3H), 3.83 (s, 3H), 6.47 (dd, $J = 3.3$, 8.0 Hz, 1H), 7.19-7.22 (m, 1H), 7.25-7.35 (m, 3H), 7.41-7.45 (m, 2H), 7.49-7.55 (m, 3H), 7.62-7.68 (m, 3H); $^{13}$C NMR δ 13.9, 22.2, 31.0, 32.1, 36.9, 53.5, 69.4, 69.6, 105.9, 109.3, 109.3, 109.7, 115.6, 120.8, 122.1, 125.3, 125.6, 127.5, 127.6, 128.9, 129.0, 129.2, 129.4, 129.9, 130.1, 131.0, 131.3, 131.3, 131.3, 131.6, 132.4, 132.7, 133.9, 134.9, 136.1, 165.2, 165.2; $^{31}$P NMR δ 31.6; HRMS (ESI positive) m/z calc for C$_{35}$H$_{34}$ClNa$_2$O$_8$P$_2$ ([M+Na$^+$]): 595.1412. Found: 595.1407.

**Dimethyl 4-pentyl-5-phenyl-1-(4-phenylphenyl)-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3ga):** a white solid; mp 146 °C; IR (CH$_2$Cl$_2$) 2924, 1737, 1216, 1205, 694, 506 cm$^{-1}$; $^1$H NMR δ 0.78 (t, $J = 6.9$ Hz, 3H), 0.83-0.90 (m, 1H), 1.08-1.22 (m, 4H), 1.45-1.52 (m, 1H), 2.94-3.07 (m, 2H), 3.49 (s, 3H), 3.84 (s, 3H), 6.56 (dd, $J = 3.3$, 8.3 Hz, 1H), 7.13-7.17 (m, 1H), 7.25-7.29 (m, 1H), 7.38-7.47 (m, 5H), 7.50-7.55 (m, 3H), 7.61-7.70 (m, 3H), 7.74-7.78 (m, 4H); $^{13}$C NMR δ 13.9, 22.3, 31.1, 32.1, 32.3, 32.4, 52.3, 52.7, 125.8, 125.9, 127.1, 127.3, 127.6, 127.9, 128.8, 128.9, 129.0, 129.7, 129.7, 129.8, 129.8, 130.0, 130.8, 131.2, 131.3, 131.4, 132.4, 132.4, 133.1, 133.1, 134.0, 134.2, 134.3, 134.8, 134.9, 135.7, 136.1, 140.1, 140.2, 140.6, 140.7, 141.2, 141.8, 142.0, 145.6, 145.7, 167.4, 167.4, 167.9; $^{31}$P NMR δ 31.7; HRMS (ESI positive) m/z calc for C$_{35}$H$_{34}$ClNa$_3$O$_{10}$P ([M+Na$^+$]): 637.2114. Found: 637.2110.

**Dimethyl 4-pentyl-5-phenyl-1-thienyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3ha):** a pale yellow oil; IR (CH$_2$Cl$_2$) 2924, 2360, 1737, 1437, 1205, 695 cm$^{-1}$; $^1$H NMR δ 0.76-0.84 (m, 4H), 1.07-1.18 (m, 4H), 1.45 (br, 1H), 3.00-3.05 (m, 2H), 3.60 (s, 3H), 3.84 (s, 3H), 6.51 (dd, $J = 3.1$, 8.0 Hz, 1H), 7.07 (br, 1H), 7.18-7.20 (m, 1H), 7.24-7.27 (m, 1H), 7.30-7.33 (m, 1H), 7.41-7.45 (m, 2H), 7.51-7.56 (m, 2H), 7.62-7.68 (m, 3H); $^{13}$C NMR δ 13.9, 22.2, 30.1, 32.1, 32.3, 32.4, 52.5, 52.7, 125.7, 126.8, 126.9, 127.6, 127.6, 127.9, 128.9, 128.9, 129.6, 129.7, 130.0, 130.0, 131.3, 131.4, 132.4, 132.5, 133.3, 133.3, 134.9, 140.1, 140.3, 140.3, 140.6, 146.8, 146.9, 167.1, 167.2, 167.5; $^{31}$P NMR δ 31.7; HRMS (ESI positive) m/z calc for C$_{35}$H$_{34}$Na$_2$O$_5$PS ([M+Na$^+$]): 567.1366. Found: 567.1365.

**2,3-Bis(hydroxymethyl)-4-pentyl-1,5-diphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3ab):** a colorless solid; mp 178 °C; IR (CH$_2$Cl$_2$) 3298, 2926, 1439, 1183, 1010, 704, 553 cm$^{-1}$; $^1$H NMR δ 0.58 (br, 1H), 0.69-0.72 (m, 3H), 0.99-1.15 (m, 4H), 1.24-1.28 (m, 2H), 1.79 (br, 1H), 2.80-2.86 (m, 1H), 2.93-2.98 (m,
4-Pentyl-1,5-diphenyl-2,3-dipropyl-5H-dibenzo[b,d]phosphate 5-oxide (3ac): a white solid; mp 86 °C; IR (CH₂Cl₂) 2924, 2853, 1457, 1204, 706 cm⁻¹; ¹H NMR δ 6.30-0.3 m (m, 2H), 6.13 (dd, J = 3.0, 8.0 Hz, 1H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 7.18 (dt, Jₕ = 3.2 Hz, Jᵢ = 7.3 Hz, 1H), 7.60-7.31 (m, 2H), 7.38-7.41 (m, 2H), 7.48-7.55 (m, 2H); ¹³C NMR δ 13.9, 22.4, 29.7, 31.6, 32.2, 58.2, 58.3, 59.7, 125.3, 125.4, 128.3, 128.6, 128.7, 128.8, 129.2, 129.3, 129.4, 129.4, 129.5, 129.6, 131.2, 131.3, 131.4, 132.2, 132.9, 137.9, 138.0, 139.0, 139.6, 140.1, 140.2, 142.0, 142.2, 145.4, 145.5; ³¹P NMR δ 33.6; HRMS (ESI positive) m/z calcd for C₃₁H₃₁N₉O₃P ([M+Na⁺]): 505.1903. Found: 505.1903.

4-Pentyl-1,2,3,5-tetraphenyl-5H-dibenzo[b,d]phosphate 5-oxide (3ad): a white solid; mp >300 °C; IR (CH₂Cl₂) 2923, 2359, 1738, 1204, 700, 436 cm⁻¹; ¹H NMR δ 0.48-0.57 (m, 4H), 0.72-0.88 (m, 4H), 1.13-1.22 (m, 1H), 2.58 (dt, Jₛ = 4.5 Hz, Jᵢ = 12.7 Hz, 1H), 2.84 (dt, Jₛ = 4.5 Hz, Jᵢ = 12.7 Hz, 1H), 6.26 (dd, J = 3.3, 8.0 Hz, 1H), 6.64-6.66 (m, 1H), 6.77-6.90 (m, 5H), 7.00-7.15 (m, 6H), 7.17-7.22 (m, 4H), 7.25-7.28 (m, 1H), 7.43-7.47 (m, 2H), 7.51-7.54 (m, 1H), 7.59-7.62 (m, 1H), 7.79-7.83 (m, 2H); ¹³C NMR δ 13.6, 21.8, 30.0, 31.9, 32.5, 32.6, 125.2, 125.3, 125.6, 126.3, 126.4, 126.6, 126.7, 127.1, 127.1, 127.3, 128.2, 128.4, 128.5, 128.6, 129.4, 129.5, 130.1, 130.2, 130.4, 130.5, 131.2, 131.2, 131.5, 131.6, 131.9, 131.9, 132.0, 132.1, 132.7, 133.7, 133.9, 134.8, 136.4, 136.4, 137.6, 138.7, 138.9, 139.2, 139.5, 142.4, 142.5, 142.7, 142.8, 144.8, 144.9, 147.6; ³¹P NMR δ 32.9; HRMS (ESI positive) m/z calcd for C₄₁H₃₅NaO₅ ([M+Na⁺]) : 529.2631. Found: 529.2632.

2,3-Bis(4-methoxyphenyl)-4-pentyl-1,5-diphenyl-5H-dibenzo[b,d]phosphate 5-oxide (3ae): a white solid; mp 228 °C; IR (CH₂Cl₂) 2925, 2360, 1608, 1514, 1246, 1203, 703 cm⁻¹; ¹H NMR δ 0.45-0.54 (m, 1H), 0.56 (t, J = 6.5 Hz, 3H), 0.73-0.88 (m, 4H), 1.11-1.21 (m, 1H), 2.58 (dt, Jₛ = 4.6 Hz, Jᵢ = 12.6 Hz, 1H), 2.82 (dt, Jₛ = 4.6 Hz, Jᵢ = 12.6 Hz, 1H), 3.59 (s, 3H), 3.70 (s, 3H), 6.22 (dd, J = 3.4, 8.1 Hz, 1H), 6.36-6.41 (m, 2H), 6.53-6.58 (m, 2H), 6.67-6.70 (m, 2H), 6.77 (dd, J = 2.1, 8.4 Hz, 1H), 6.97 (dd, J = 2.1, 6.4 Hz, 1H), 6.99-7.01 (m, 1H), 7.05-7.09 (m, 1H), 7.16-7.22 (m, 4H), 7.26-7.29 (m, 1H), 7.42-7.46 (m, 2H), 7.50-7.53 (m, 1H), 7.59 (dd, J = 3.7, 7.1 Hz, 1H), 7.78-7.82 (m, 2H); ¹³C NMR δ 13.7, 21.9, 30.0, 31.9, 32.6, 54.8, 55.0, 55.0, 112.0, 112.1, 112.6, 112.9, 113.9, 125.2, 125.3, 127.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 129.3, 129.4, 130.1, 130.2, 131.1, 131.2, 131.3, 131.4, 131.5, 131.5, 131.6,
131.8, 131.8, 131.9, 132.1, 132.6, 132.6, 133.9, 134.7, 136.8, 136.9, 138.5, 139.8, 142.4, 142.8, 142.9, 145.2, 157.1, 157.8; $^{31}$P NMR $\delta$ 33.0; HRMS (ESI positive) m/z calcd for C$_{43}$H$_{39}$NaO$_3$P ([M+Na]$^+$): 657.2529. Found: 657.2526.

2,3-Bis(4-bromophenyl)-4-pentyl-1,5-diphenyl-5$H$-dibenzo[b,d]phosphole 5-oxide (3af): a white solid; mp 237 °C; IR (CH$_2$Cl$_2$) 2928, 1489, 1201, 1011, 704, 527 cm$^{-1}$; $^1$H NMR $\delta$ 0.46-0.52 (m, 1H), 0.59 (t, $J = 6.8$ Hz, 3H), 0.76-0.89 (m, 4H), 1.09-1.16 (m, 1H), 2.49-2.55 (m, 1H), 2.79-2.85 (m, 1H), 6.23-6.26 (m, 1H), 6.50-6.52 (m, 1H), 6.65-6.67 (m, 1H), 6.75-6.77 (m, 1H), 6.93-6.95 (m, 1H), 6.98-7.02 (m, 3H), 7.07-7.11 (m, 1H), 7.15-7.32 (m, 7H), 7.43-7.47 (m, 2H), 7.52-7.55 (m, 1H), 7.59-7.62 (m, 1H), 7.76-7.81 (m, 2H); $^{13}$C NMR $\delta$ 13.7, 22.0, 25.7, 30.2, 32.0, 32.5, 32.6, 120.3, 121.0, 125.4, 125.5, 127.6, 128.6, 128.7, 128.8, 128.8, 128.9, 129.0, 129.6, 129.7, 130.0, 130.0, 130.1, 130.1, 130.3, 130.7, 131.0, 131.0, 131.6, 131.7, 131.9, 132.0, 132.0, 132.0, 132.1, 132.2, 132.2, 132.8, 132.9, 132.9, 134.0, 134.8, 136.5, 136.5, 137.6, 137.6, 138.0, 139.1, 139.3, 139.5, 141.3, 141.4, 142.1, 142.3, 144.9, 146.2, 146.2; $^{31}$P NMR $\delta$ 32.7; HRMS (ESI positive) m/z calcd for C$_{41}$H$_{33}$Br$_2$NaOP ([M+Na]$^+$): 753.0528. Found: 753.0522.

2,3-Bis(4,4,4,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-pentyl-1,5-diphenyl-5$H$-dibenzo[b,d]phosphole 5-oxide (3ag): a white solid; mp 96 °C; IR (CH$_2$Cl$_2$) 2927, 2360, 2189, 1359, 1202, 1144, 417 cm$^{-1}$; $^1$H NMR $\delta$ 0.44-0.56 (m, 4H), 0.71-0.94 (m, 5H), 1.27 (s, 12H), 1.31 (s, 12H), 2.49-2.55 (m, 1H), 2.76-2.82 (m, 1H), 6.18 (dd, $J = 3.4$, 8.2 Hz, 1H), 6.67-6.68 (m, 1H), 6.81-6.83 (m, 1H), 6.88-6.90 (m, 1H), 6.99-7.01 (m, 1H), 7.05-7.09 (m, 1H), 7.16-7.27 (m, 6H), 7.40-7.47 (m, 3H), 7.49-7.61 (m, 4H), 7.76-7.81 (m, 3H); $^{13}$C NMR $\delta$ 13.8, 22.0, 25.0, 29.7, 29.8, 30.3, 30.7, 38.4, 39.7, 41.9, 51.1, 51.5, 59.7, 67.8, 83.7, 83.8, 97.2, 97.3, 98.8, 100.0, 102.9, 103.8, 110.7, 116.4, 118.1, 127.3, 128.4, 128.5, 128.5, 128.6, 128.7, 128.8, 129.3, 129.4, 129.5, 129.6, 129.7, 129.7, 129.9, 130.1, 130.1, 130.9, 131.2, 131.5, 131.6, 131.6, 131.9, 132.1, 132.8, 133.1, 133.4, 133.7, 133.9, 134.7, 139.5; $^{31}$P NMR $\delta$ 33.0; HRMS (ESI positive) m/z calcd for C$_{53}$H$_{57}$B$_2$NaO$_3$P ([M+Na]$^+$): 847.4088. Found: 847.4095.

4-Pentyl-1,5-diphenyl-2,3-bis(thien-2-yl)-5$H$-dibenzo[b,d]phosphole 5-oxide (3ah): a brown oil; IR (CH$_2$Cl$_2$) 2925, 1738, 1458, 1203, 701, 520 cm$^{-1}$; $^1$H NMR $\delta$ 0.60-0.66 (m, 4H), 0.84-0.95 (m, 3H), 1.17-1.37 (m, 2H), 2.72 (dt, $J_d = 4.7$ Hz, $J_t = 12.9$ Hz, 1H), 2.91 (dt, $J_d = 4.7$ Hz, $J_t = 12.9$ Hz, 1H), 6.26 (dd, $J = 3.3$, 8.2 Hz, 1H), 6.41 (dd, $J = 1.1$, 3.4 Hz, 1H), 6.57 (dd, $J = 3.4$, 5.1 Hz, 1H), 6.75 (dd, $J = 1.1$, 3.5 Hz, 1H), 6.83 (dd, $J = 3.5$, 5.2 Hz, 1H), 6.96 (dd, $J = 0.9$, 5.0 Hz, 1H), 7.08-7.12 (m, 2H), 7.17 (dd, $J = 1.1$, 5.1 Hz, 1H), 7.20-7.35 (m, 5H), 7.43-7.47 (m, 2H), 7.52-7.55 (m, 1H), 7.59-7.63 (m, 1H), 7.76-7.80 (m, 2H); $^{13}$C NMR $\delta$ 13.8, 22.0, 22.4, 30.8, 32.1, 43.8, 123.1, 123.9, 124.2, 125.5, 125.6, 126.0, 126.0, 126.0, 126.2, 127.6, 127.8, 128.3, 128.4, 128.5, 128.7, 128.7, 128.8, 128.8, 128.8, 128.9, 128.9, 129.3, 129.6, 129.9, 130.0, 130.9, 131.2, 131.4, 131.5, 131.6, 131.9, 132.1, 132.1, 132.8, 134.0, 137.8, 139.2, 139.5, 139.8, 146.4, 146.7; $^{31}$P NMR $\delta$ 32.5; HRMS (ESI positive) m/z calcd for
Methyl 4-pentyl-1,2,5-triphenyl-5H-dibenzo[b,d]phosphole-3-carboxylate 5-oxide (3ai) and methyl 4-pentyl-1,3,5-triphenyl-5H-dibenzo[b,d]phosphole-2-carboxylate 5-oxide (4ai): a pale yellow solid; mp 131 °C; IR (CH2Cl2) 2925, 1733, 1206, 701, 444 cm⁻¹; ¹H NMR δ 0.46-0.59 (m, 4H), 0.76-0.95 (m, 8H), 1.06-1.23 (m, 5H), 1.53-1.62 (m, 1H), 2.55-2.61 (m, 1H), 2.73-2.90 (m, 2H), 2.90-2.96 (m, 1H), 3.09 (s, 3H), 3.37 (s, 3H), 6.30 (dd, J = 3.4, 7.9 Hz, 1H), 6.43 (dd, J = 3.2, 7.9 Hz, 1H), 6.99-7.15 (m, 8H), 7.20-7.31 (m, 9H), 7.37-7.38 (m, 2H), 7.41-7.55 (m, 11H), 7.59-7.63 (m, 2H), 7.70-7.77 (m, 4H); ¹³C NMR δ 13.6, 13.7, 13.9, 21.8, 22.2, 29.9, 31.0, 31.8, 31.8, 31.9, 31.9, 32.3, 32.6, 32.6, 51.4, 51.7, 125.2, 125.3, 125.6, 127.0, 127.1, 127.3, 127.6, 127.7, 127.8, 127.9, 128.5, 128.5, 128.7, 128.7, 128.8, 128.8, 128.8, 128.9, 129.0, 129.1, 129.5, 129.5, 129.6, 129.7, 129.7, 130.1, 130.1, 130.6, 130.6, 130.7, 131.4, 131.4, 131.5, 131.5, 131.5, 131.7, 132.1, 132.2, 132.6, 132.8, 132.9, 132.9, 133.3, 133.3, 133.4, 133.7, 134.1, 134.5, 134.5, 135.7, 136.6, 137.6, 137.8, 138.4, 138.8, 139.0, 139.8, 140.7, 141.4, 141.4, 141.6, 141.6, 141.8, 143.1, 145.2, 145.3, 145.6, 145.6, 168.3, 169.0, 169.0; ³¹P NMR δ 32.0, 32.5; HRMS (ESI positive) m/z calcd for C₃₇H₃₁NaOPS₂ ([M+Na]⁺): 609.1446. Found: 609.1445.

4-Pentyl-1,2,5-triphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3aj): HMBC correlation was observed between carbon atom on pentyl group and hydrogen atom on benzene ring: a white solid; mp 88 °C; IR (CH2Cl2) 2922, 2359, 1739, 1466, 1365, 1204 cm⁻¹; ¹H NMR δ 0.76-0.79 (m, 3H), 1.13-1.18 (m, 5H), 1.50-1.56 (m, 1H), 2.82-2.85 (m, 2H), 6.34 (dd, J = 3.3, 8.2 Hz, 1H), 7.04-7.08 (m, 3H), 7.13-7.20 (m, 7H), 7.29-7.32 (m, 3H), 7.42-7.46 (m, 2H), 7.50-7.54 (m, 1H), 7.59-7.63 (m, 1H), 7.74-7.78 (m, 2H); ¹³C NMR δ 13.9, 22.4, 30.6, 31.7, 33.6, 33.7, 125.4, 125.5, 126.7, 127.5, 127.6, 128.5, 128.5, 128.8, 129.5, 129.6, 130.4, 130.5, 130.6, 131.1, 131.3, 131.3, 131.3, 131.4, 131.4, 132.0, 132.0, 132.6, 132.7, 133.9, 134.8, 135.5, 135.6, 139.0, 139.7, 139.9, 140.7, 145.9, 146.0, 147.8, 147.8; ³¹P NMR δ 31.9; HRMS (ESI positive) m/z calcd for C₃₅H₂₉NaOP ([M+Na]⁺): 579.2060. Found: 579.2059.

2,3-Bis(methoxycarbonyl)-4-pentyl-1-phenyl dibenzo[b,d]thiophene-5-oxide (6a): a yellow oil; IR (CH2Cl2) 2925, 2853, 1737, 1436, 1038, 702 cm⁻¹; ¹H NMR δ 0.93 (t, J = 7.3 Hz, 3H), 1.37-1.52 (m, 4H), 1.74-1.90 (m, 2H), 3.17-3.23 (m, 1H), 3.37-3.43 (m, 1H), 3.48 (s, 3H), 3.90 (s, 3H), 6.35 (d, J = 8.0 Hz, 1H), 7.18 (ddd, J = 1.0, 8.2, 8.2 Hz, 1H), 7.26-7.28 (m, 1H), 7.31-7.33 (m, 1H), 7.42 (dd, J = 7.6, 7.6 Hz, 1H), 7.47-7.52 (m, 3H), 7.94 (d, J = 7.7 Hz, 1H); ¹³C NMR δ 14.0, 22.4, 31.2, 31.4, 32.2, 52.4, 52.9, 126.0, 127.4, 128.9, 129.0, 129.1, 129.2, 129.9, 131.5, 132.4, 135.3, 136.2, 136.3, 137.2, 139.0, 143.1, 145.3, 145.9, 167.1, 167.5; HRMS (ESI positive) m/z calcd for C₂₇H₂₆NaO₃S ([M+Na]⁺): 485.1393. Found: 485.1395.
4-Pentyl-1,2,3-triphenyldibenzo[b,d]thiophene-5-oxide (6d): a white solid; mp 150 °C; IR (CH2Cl2) 2926, 1465, 1442, 1033 cm⁻¹; 1H NMR δ 0.77 (t, J = 7.1 Hz, 3H), 1.15-1.25 (m, 4H), 1.61-1.67 (m, 2H), 2.79-2.85 (m, 1H), 3.10-3.16 (m, 1H), 6.23 (d, J = 7.9 Hz, 1H), 6.71-6.75 (m, 2H), 6.79-6.87 (m, 3H), 7.01-7.03 (m, 1H), 7.06-7.18 (m, 7H), 7.20-7.25 (m, 3H), 7.35 (ddd, J = 0.5, 7.5, 7.5 Hz, 1H), 7.83 (dd, J = 0.6, 7.7 Hz, 1H); 13C NMR δ 13.9, 22.1, 30.7, 31.3, 32.1, 125.5, 125.9, 126.7, 126.8, 127.3, 127.5, 127.5, 127.6, 128.4, 128.6, 128.7, 130.0, 130.0, 130.2, 130.5, 130.5, 130.6, 132.0, 134.3, 136.8, 138.0, 138.6, 138.9, 142.2, 143.0, 143.1, 145.1, 146.9; HRMS (ESI positive) m/z calc'd for C35H30NaOS ([M+Na]+): 521.1910. Found: 521.1915.

2,3-Bis(hydroxymethyl)-4-pentyl-1-(4-tolyl)-5-(2-(4-tolylethynyl)phenyl)-5H-dibenzo[b,d]phosphole 5-oxide (8): a white solid; mp 124 °C; IR (CH2Cl2) 3369, 2922, 2852, 2360, 1634, 1465, 721 cm⁻¹; 1H NMR δ 0.69 (t, J = 7.2 Hz, 3H), 0.78-1.13 (m, 6H), 1.37-1.47 (m, 1H), 1.76 (br, 1H), 2.40 (s, 6H), 2.85-2.88 (m, 2H), 4.27-4.35 (m, 2H), 4.73-4.80 (m, 2H), 5.95 (d, J = 7.4 Hz, 1H), 6.03-6.05 (m, 1H), 6.70-6.72 (m, 2H), 6.90 (d, J = 7.4 Hz, 1H), 6.95-6.97 (m, 1H), 7.02-7.06 (m, 3H), 7.14-7.20 (m, 2H), 7.45-7.50 (m, 2H), 7.53-7.56 (m, 1H), 7.62-7.65 (m, 1H), 8.64-8.68 (m, 1H); 13C NMR δ 13.9, 21.3, 21.5, 22.4, 31.7, 32.2, 32.5, 58.4, 59.7, 85.2, 85.2, 96.4, 119.2, 125.3, 125.3, 125.5, 125.5, 128.2, 128.3, 128.3, 128.4, 128.8, 128.8, 128.9, 129.1, 129.3, 129.8, 130.6, 130.8, 131.4, 131.7, 131.7, 132.0, 132.4, 133.4, 134.0, 134.1, 135.0, 135.6, 137.3, 137.7, 137.8, 138.8, 139.5, 139.5, 140.6, 140.8, 143.5, 143.6, 144.8, 144.9; 31P NMR δ 31.0; HRMS (ESI positive) m/z calc'd for C41H39NaO3P ([M+Na]+): 633.2529. Found: 633.2525. [d]28° -10.4 (c 0.21, CHCl3, 83% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IC: 4 x 250 mm, 254 nm UV detector, rt, eluent: 2-propanol:hexane = 40:60, flow rate: 0.25 mL/min, retention time: 40.1 min for minor isomer and 54.9 min for major isomer).

Dimethyl 1-(dibenzo[b,d]thiophen-2-yl)-4-pentyl-5-phenyl-5H-dibenzo[b,d]phosphole-2,3-dicarboxylate 5-oxide (3ia): a white solid; mp 131 °C; IR (CH2Cl2) 2953, 1737, 1437, 1206, 736, 520 cm⁻¹; 1H NMR δ 0.78-0.81 (m, 3H), 0.84-0.92 (m, 1H), 1.09-1.24 (m, 4H), 1.44-1.57 (m, 1H), 2.95-3.10 (m, 2H), 3.40 (d, J = 2.3 Hz, 3H), 3.84 (d, J = 1.6 Hz, 3H), 6.41-6.43 (m, 1H), 7.02-7.06 (m, 1H), 7.21-7.25 (m, 1H), 7.40-7.57 (m, 1H), 7.61-7.64 (m, 1H), 7.67-7.73 (m, 2H), 7.91-7.94 (m, 1H), 7.99-8.01 (m, 1H), 8.10-8.18 (m, 2H); 13C NMR δ 13.8, 22.2, 31.0, 32.1, 32.3, 52.3, 52.6, 121.9, 122.0, 121.1, 122.3, 122.9, 123.0, 123.2, 123.5, 124.6, 124.8, 125.7, 125.8, 125.8, 125.9, 127.3, 127.3, 127.8, 127.9, 128.8, 129.7, 129.7, 129.8, 129.8, 130.0, 130.0, 130.1, 131.2, 131.2, 131.3, 131.3, 131.3, 132.4, 133.2, 133.3, 133.9, 133.9, 134.2, 134.3, 134.8, 134.8, 134.9, 135.1, 135.2, 135.6, 135.7, 136.0, 136.2, 139.8, 139.8, 139.9, 140.0, 140.4, 140.4, 140.5, 140.5, 140.6, 140.7, 141.9, 142.0, 142.1, 142.1, 145.7, 145.8, 145.8, 145.8, 167.3, 167.3, 167.3, 167.4, 167.4, 167.8; 31P NMR δ 31.7; HRMS (ESI positive) m/z calc'd for C39H33NaO5PS ([M+Na]+): 667.1679. Found: 667.1678.

1-(Dibenzo[b,d]thiophen-2-yl)-4-pentyl-2,3,5-triphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3id): a
white solid; mp 259 °C; IR (CH₂Cl₂) 2926, 1458, 1200, 729, 701, 527 cm⁻¹; ¹H NMR δ 0.53-0.59 (m, 4H), 0.72-0.86 (m, 4H), 1.16-1.24 (m, 1H), 2.57-2.64 (m, 1H), 2.82-2.90 (m, 1H), 6.26-6.29 (m, 1H), 6.66-7.17 (m, 13H), 7.29-7.56 (m, 5H), 7.58-7.63 (m, 1H), 7.68-7.75 (m, 1H), 7.81-8.07 (m, 5H); ¹³C NMR δ 13.8, 13.8, 21.1, 30.2, 30.2, 32.0, 32.0, 32.7, 32.7, 118.2, 121.7, 121.9, 122.7, 122.9, 123.0, 123.1, 123.3, 123.4, 124.5, 124.6, 125.3, 125.4, 125.4, 125.4, 125.4, 125.8, 125.8, 126.5, 126.6, 126.6, 126.9, 126.9, 126.9, 127.0, 127.2, 127.2, 127.5, 128.6, 128.6, 128.6, 128.7, 128.7, 128.8, 129.0, 129.0, 129.6, 129.6, 129.6, 129.7, 129.7, 130.3, 130.4, 130.5, 130.5, 130.5, 130.6, 131.3, 131.5, 131.5, 131.6, 131.7, 131.7, 131.8, 131.8, 132.1, 132.1, 132.1, 132.1, 132.3, 132.3, 132.3, 132.9, 133.0, 134.0, 134.1, 134.9, 134.9, 135.5, 135.6, 135.9, 135.9, 136.0, 136.1, 136.1, 136.2, 136.2, 138.3, 138.4, 138.8, 138.8, 139.1, 139.1, 139.2, 139.3, 139.8, 134.0, 142.4, 142.5, 142.6, 142.6, 143.0, 143.0, 143.1, 143.1, 145.1, 145.2; ³¹P NMR δ 32.9; HRMS (ESI positive) m/z calcd for C₄₁H₅₀NaOPS ([M+Na⁺]: 703.2195. Found: 703.2190.

2-Dibenzo[b,d]thiophen-2-yl-4-penty1-1,5-diphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3ak): a white solid; mp 104 °C; IR (CH₂Cl₂) 3054, 2927, 1463, 1198, 703, 418 cm⁻¹; ¹H NMR δ 0.73-0.80 (m, 4H), 1.12-1.22 (m, 4H), 1.56-1.60 (m, 1H), 2.86-2.89 (m, 2H), 6.38 (dd, J = 3.2, 8.0 Hz, 2H), 7.08-7.15 (m, 2H), 7.19-7.31 (m, 6H), 7.45-7.55 (m, 5H), 7.59-7.65 (m, 2H), 7.76-7.83 (m, 3H), 7.86 (s, 1H), 7.98-8.00 (m, 1H); ¹³C NMR δ 14.0, 22.4, 22.4, 30.7, 30.7, 31.7, 33.7, 33.7, 121.5, 121.8, 122.6, 122.9, 123.5, 124.4, 125.4, 125.5, 126.8, 126.8, 127.0, 127.7, 128.4, 128.4, 128.5, 128.6, 128.8, 128.9, 129.5, 129.6, 130.4, 130.5, 130.7, 130.8, 131.1, 131.4, 131.5, 131.6, 131.7, 131.9, 132.0, 132.0, 132.0, 132.7, 134.8, 135.0, 135.4, 135.7, 135.8, 137.1, 138.0, 138.9, 139.7, 142.5, 142.5, 145.9, 146.0, 146.1, 146.1, 147.5; ³¹P NMR δ 31.9; HRMS (ESI positive) m/z calcd for C₄₁H₃₃NaOPS ([M+Na⁺]): 627.1882. Found: 627.1879.

1,2-Bis(dibenzo[b,d]thiophen-2-yl)ethyne (2I): a pale grey solid; mp 283 °C; IR (CH₂Cl₂) 1739, 1364, 1217, 417 cm⁻¹; ¹H NMR (DMSO-d₆) δ 7.47-7.51 (m, 4H), 7.65 (dd, J = 1.6, 8.4 Hz, 2H), 7.92-7.95 (m, 2H), 7.98 (d, J = 8.3 Hz, 2H), 8.34-8.38 (m, 2H), 8.48 (d, J = 1.2 Hz, 2H); ¹³C NMR (CDCl₃ with CS₂) δ 113.8, 113.8, 113.9, 115.1, 127.8, 128.0, 128.5, 133.1, 136.3, 152.3, 154.7, 159.4, 170.8; HRMS (ESI positive) m/z calcd for C₂₆H₁₅S₂ ([M+H⁺]: 361.0610. Found: 361.0605.

1,2-Bis(8-hept-1-yl)-dibenzo[b,d]thiophen-2-yl)ethyne (2m): a pale yellow solid; mp 83 °C; IR (CH₂Cl₂) 2924, 2852, 1736, 1457, 811 cm⁻¹; ¹H NMR δ 0.89 (t, J = 7.2 Hz, 6H), 1.25-1.42 (m, 16H), 1.70-1.76 (m, 4H), 2.80 (t, J = 7.8 Hz, 4H), 7.83 (dd, J = 1.5, 8.2 Hz, 2H), 7.64 (dd, J = 1.5, 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 8.00 (s, 2H), 8.38 (s, 2H); ¹³C NMR δ 14.1, 22.7, 29.2, 29.3, 31.8, 31.9, 36.0, 89.6, 119.3, 121.3, 122.5, 122.9, 124.8, 128.2, 129.5, 135.2, 135.8, 137.0, 139.8, 139.9; HRMS (ESI positive) m/z calcd for C₄₀H₃₄S₂ ([M+H⁺]): 587.2801. Found: 587.2801.

2,3-Bis(dibenzo[b,d]thiophen-2-yl)-4-penty1-1,5-diphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3al): a
2.3-Bis(8-(hept-1-yl)dibenzo[b,d]thiophen-2-yl)-4-pentyl-1,5-diphenyl-5H-dibenzo[b,d]phosphole 5-oxide (3am): a colorless solid; mp 61 °C; IR (CH₂Cl₂) 2953, 2925, 2853, 1438, 1278, 1202, 703, 418 cm⁻¹; ¹H NMR δ 0.43-0.51 (m, 4H), 0.65-0.94 (m, 16H), 1.21-1.38 (m, 12H), 1.64-1.74 (m, 3H), 2.47-2.65 (m, 1H), 2.65-2.69 (m, 4H), 2.84-2.97 (m, 1H), 6.27-6.33 (m, 1H), 6.92-6.97 (m, 1H), 7.00-7.31 (m, 10H), 7.45-7.90 (m, 13H), 7.90-8.00 (m, 1H); ¹³C NMR δ 5.8, 9.1, 10.1, 10.8, 12.6, 14.1, 14.1, 14.1, 21.9, 22.6, 22.7, 22.7, 25.4, 25.8, 28.9, 29.2, 29.2, 29.2, 29.2, 29.3, 29.3, 29.3, 31.0, 31.8, 31.9, 33.4, 35.7, 35.9, 36.0, 39.2, 41.0, 53.4, 55.7, 63.9, 67.0, 69.0, 83.2, 106.3, 107.6, 111.7, 114.5, 121.5, 122.6, 124.8, 124.8, 126.1, 127.7, 128.9, 129.6, 130.1, 131.6, 135.8, 135.9, 137.0, 140.0, 140.7, 143.0, 143.8, 148.0, 148.4, 148.7, 153.6, 158.3, 159.1, 165.7, 168.6, 168.8, 172.1, 172.8, 176.6, 176.7, 177.6, 179.0; ³¹P NMR δ 33.1; HRMS (ESI positive) m/z calcd for C₅₃H₅₆NaOPS⁺ ([M+Na]⁺): 1005.4263. Found: 1005.4260.

Synthesis of 4-Pentyl-1,5-diphenyl-2,3-dipropyl-5H-dibenzo[b,d]phosphole 5-sulfide (9). Dibenzophosphole oxide 3ac (33.8 mg, 0.068 mmol) and Lawesson’s reagent (54.9 mg, 0.136 mmol, 2 equiv) were dissolved in toluene (4.9 mL), and the mixture was heated under reflux for 1 h. After removal of solvent under reduced pressure, the obtained crude products were purified by silica gel column (hexane:acetone = 5:1) to give analytically pure 9 (34.8 mg, 0.067 mmol, 98%) as a white solid; mp 147 °C; IR (CH₂Cl₂) 2922, 2851, 1634, 1463, 703, 418 cm⁻¹; ¹H NMR δ 0.60-0.67 (m, 1H), 0.74 (t, J = 7.3 Hz, 3H), 0.80 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.3 Hz, 3H), 1.06-1.18 (m, 3H), 1.24-1.28 (m, 1H), 1.32-1.40 (m, 2H), 1.44-1.62 (m, 3H), 2.34-2.37 (m, 2H), 2.56-2.59 (m, 2H), 2.68 (dt, J₁ = 4.4 Hz, J₂ = 13.0 Hz, 1H), 3.15 (dt, J₁ = 4.4 Hz, J₂ = 13.0 Hz, 1H), 5.99-6.01 (m, 1H), 6.98-7.01 (m, 1H), 7.11-7.15 (m, 1H), 7.29-7.33 (m, 2H), 7.35-7.39 (m, 2H), 7.43-7.55 (m, 5H), 7.77-7.82 (m, 2H); ¹³C NMR δ 14.1, 14.9, 15.1, 22.5, 24.6, 25.1, 30.9, 31.2, 32.0, 32.1, 32.5, 32.8, 125.0, 125.1, 127.8, 128.3, 128.4, 128.5, 128.6, 128.8, 129.0, 129.3, 129.6, 129.8, 131.4, 131.5, 131.5, 131.6, 131.7, 131.9, 131.9, 132.1, 132.1, 136.7, 137.4, 137.4, 137.5, 137.5, 140.5, 141.3, 141.4, 142.3, 142.4, 144.6, 144.7, 145.8, 145.8; ³¹P NMR
δ 39.0; HRMS (ESI positive) m/z calcd for C_{35}H_{39}NaPS ([M+Na]^+): 545.2402. Found: 545.2404.

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REFERENCES AND NOTES


