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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] helical[5] and ladder-type[6] 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 phosphanylation using $(Me_3Sn)_2PPh$ and 1,1'-azobis(cyclohexane-1-carbonitrile (V-40),[3f] and radical cyclization with triethylborane and oxygen[6b] were reported. As for catalytic approaches, Pd-catalyzed direct arylation initiated by C-H or/and C-P

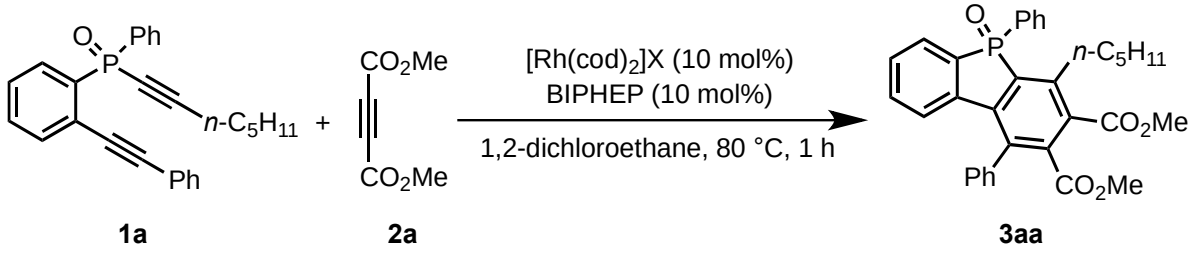
bond cleavage[7] and Pd-catalyzed dehydrogenative cyclization[8] were recently disclosed. However, most of these examples are the synthesis of non- or monosubstituted DBP oxides. Therefore, a conventional approach to the synthesis of multi-substituted DBP oxides is strongly desired.

Transition-metal-catalyzed [2+2+2] cycloaddition is a reliable and atom-economical protocol for the construction of condensed polycyclic ring systems.[9] The dibenzoheteroles, such as carbazoles,[10] dibenzofurans,[11] and dibenzosiloles[12] 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 tetraynes for the synthesis of helical compounds containing DBP skeleton.[5a,b] We have comprehensively studied [2+2+2] cycloaddition of various substrates with alkyne motifs,[13] 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.[14] 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,[14] 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 (BF_4) and hexafluorophosphate (PF_6) gave the comparable good yields (Entries 1 and 2). Trifluoromethanesulfonate (OTf) and hexafluoroantimonate (SbF_6) 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**



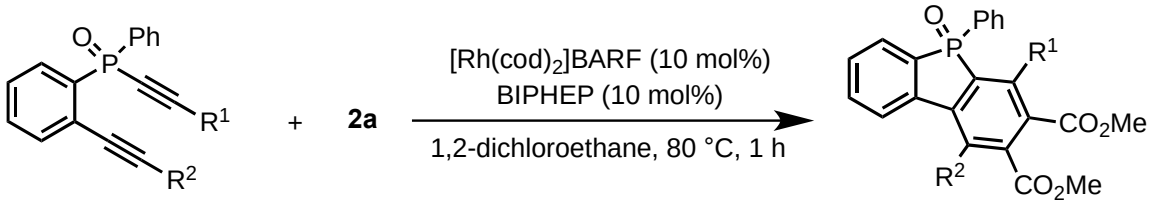
1a **2a** **3aa**

Entry [a]	X	Yield (%)
1	BF_4	78
2	PF_6	73
3	OTf	42
4	SbF_6	46
5	BARF	85

[a] Diyne/alkyne was 1/3. Diyne **1a** was added dropwise to a 1,2-dichloroethane solution of the Rh catalyst and alkyne **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**



1 **3**

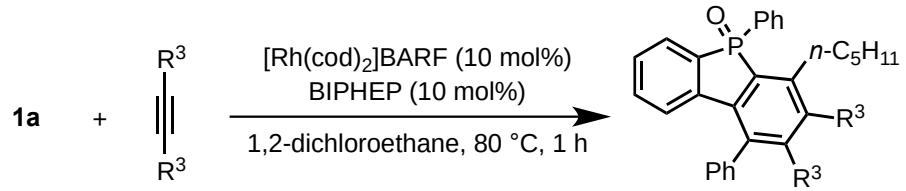
Entry [a]	Diyne	R^1	R^2	Yield (%)
1	**1b**	Ph	*n*-C_5H_{11}	trace (**3ba**)
2	**1c**	Ph	Ph	27 (**3ca**)
3	**1d**	*n*-C_5H_{11}	C_6H_4(*p*-Me)	86 (**3da**)
4	**1e**	*n*-C_5H_{11}	C_6H_4(*p*-OMe)	84 (**3ea**)
5	**1f**	*n*-C_5H_{11}	C_6H_4(*p*-Cl)	80 (**3fa**)

6	**1g**	*n*-C_5H_{11}	C_6H_4(*p*-Ph)	86 (**3ga**)
7	**1h**	*n*-C_5H_{11}	2-thienyl	91 (**3ha**)

[a] 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** containg two thiophenyl groups was obtained in 90% yield (Entry 7).

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

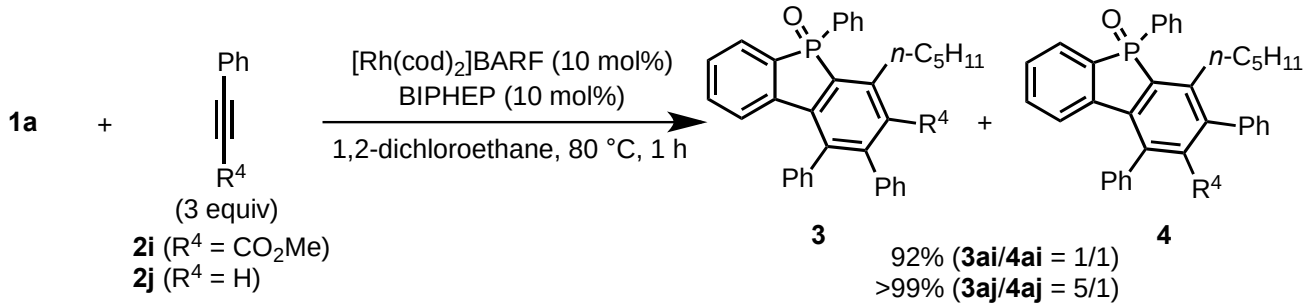


2 **3**

Entry[a]	Alkyne	R^3	Yield (%)
1	**2b**	CH_2OH	91 (**3ab**)
2	**2c**	*n*-C_3H_7	93 (**3ac**)
3	**2d**	Ph	81 (**3ad**)
4	**2e**	C_6H_4(*p*-OMe)	77 (**3ae**)
5	**2f**	C_6H_4(*p*-Br)	57 (**3af**)
6	**2g**	C_6H_4(*p*-Bpin)	58 (**3ag**)
7	**2h**	2-thienyl	90 (**3ah**)

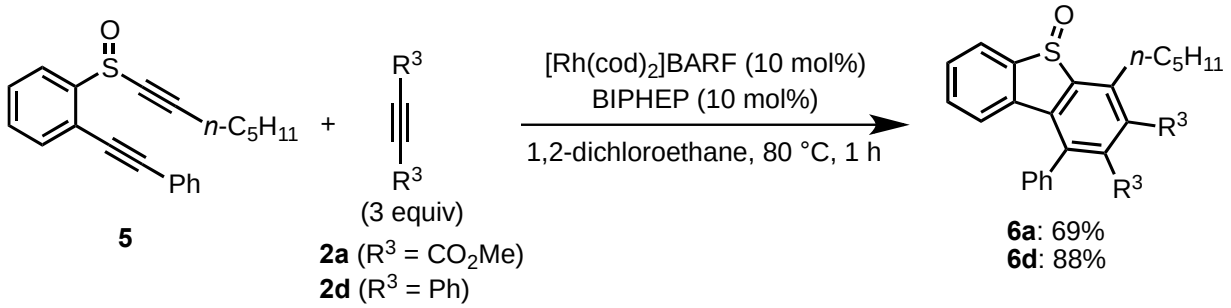
[a] Diyne/alkyne was 1/3. Diyne **1a** was added dropwise to a solution of the Rh catalyst and alkyne.

The cycloaddition using unsymmetrical alkynes also proceeded under the same reaction conditions (Scheme 1). The reaction of **1a** with ethyl phenylpropiolate (**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.



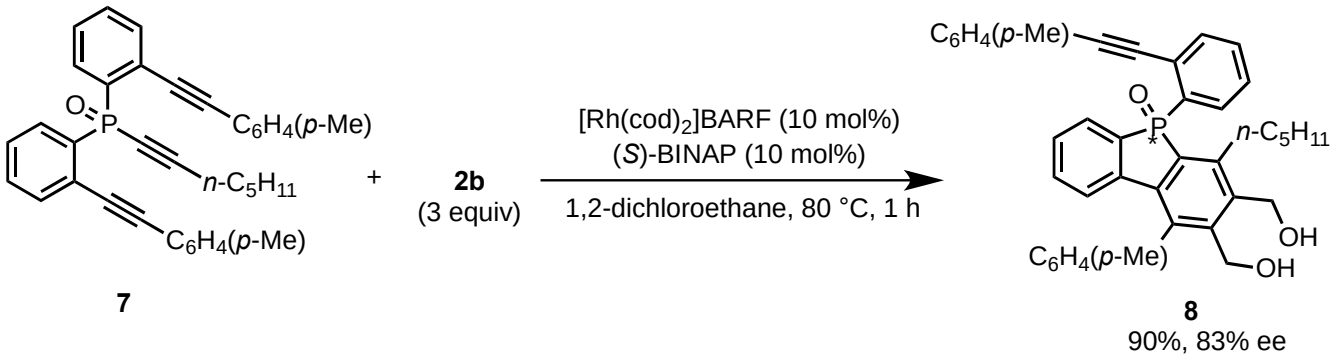
Scheme 1. Cycloaddition of diyne **1a** with unsymmetrical alkynes **2i** and **2j**

As sulfur analogue of phosphorylbenzene-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.



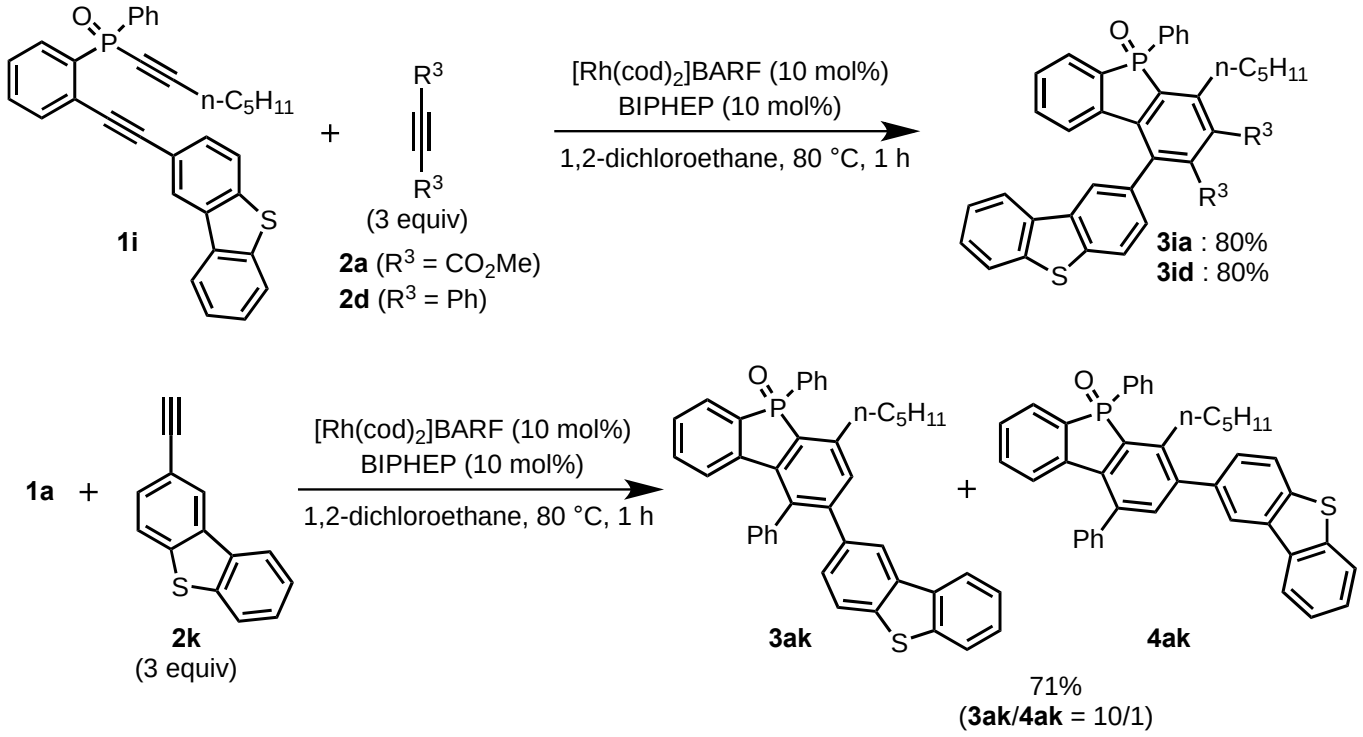
Scheme 2. Synthesis of dibenzothiophene 5-oxide derivatives

The asymmetric desymmetrization using [2+2+2] cycloaddition has already been reported: the reaction of symmetrical dialkynyl alcohol[15] or dialkynylphosphine oxide[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.[17] Against this background, we next focused on the asymmetric desymmetrization using phosphorylbenzene-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,[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

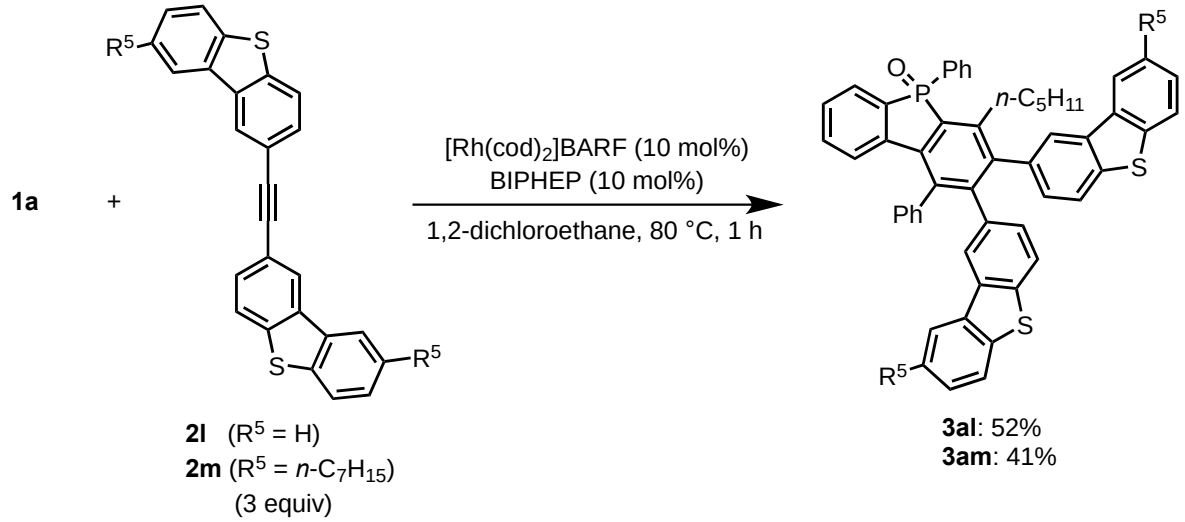
In the light of the application of DBP oxide derivatives, we synthesized the DBP oxides possessing dibenzothiophene(s) (DBT) as substituent(s) (Schemes 4 and 5). The reaction of diyne **1i**, which has dibenzo[*b*,*d*]thiophen-2-yl group on one of its alkyne termini, proceeded to give the desired DBP 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-dibenzoheteroles

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.



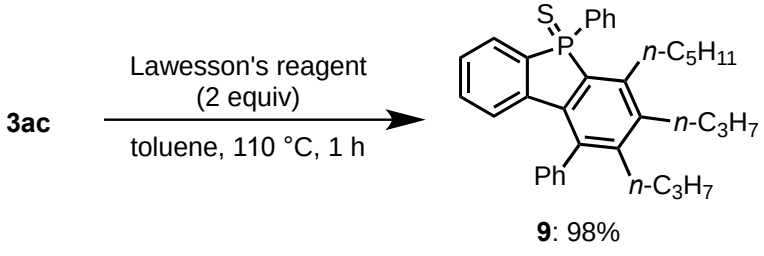
Scheme 5. Synthesis of ter(dibenzoheterolyl)s

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 λ_{max} of these compounds were observed at 317.6-338.0 nm. There is no significant difference in the value of λ_{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**

Entry	Compound	UV-vis λ_{max} (nm) / log ε
1	**3ad**	338.0 / 3.45
2	**3id**	332.0 / 3.21
3	**3ak**	317.6 / 3.65
4	**3al**	332.2 / 3.09

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 (^{1}H NMR, 495.13 MHz; ^{13}C NMR, 124.5 MHz; ^{31}P NMR, 200.43 MHz) using TMS as an internal standard, $CDCl_3$ and DMSO-d_6 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 (CH_2Cl_2) 2924, 2193, 1438, 1201, 758, 691 cm^{-1}; ^{1}H 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, J_d = 3.6 Hz, J_t = 7.2 Hz, 2H), 7.22-7.61 (m, 11H), 7.81-7.85 (m, 2H), 8.26-8.31 (m, 1H); ^{13}C NMR δ 13.9, 19.9, 19.9, 22.1, 27.3, 27.3, 31.1, 73.8, 75.2, 87.7, 87.7, 97.5, 109.2, 109.5, 122.8, 125.6, 125.6, 128.0, 128.1, 128.3, 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, 133.4, 133.6, 133.7, 133.7, 134.1; ^{31}P NMR δ 5.9; HRMS (ESI positive) *m/z* calcd for $C_{27}H_{25}NaOP$ ([M+Na]$^+$): 419.1535. Found: 419.1527.

(2-(Hept-1-yn-1-yl)phenyl)(phenyl)(phenylethynyl)phosphine oxide (1b): a yellow oil; IR (CH_2Cl_2) 2924, 2175, 1436, 846, 691, 436 cm^{-1}; ^{1}H 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); ^{13}C NMR δ 13.8, 19.6, 22.1, 27.7, 31.1, 78.7, 78.8, 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, 132.9, 133.2, 133.2, 133.6, 133.7, 133.9; ^{31}P NMR δ 7.3; HRMS (ESI positive) *m/z* calcd for $C_{27}H_{25}NaOP$ ([M+Na]$^+$): 419.1535. Found: 419.1533.

Phenyl(phenylethynyl)(2-(phenylethynyl)phenyl)phosphine oxide (1c): a pale yellow oil; IR (CH_2Cl_2)

2922, 2359, 1739, 1202, 690, 407 cm^{-1}; ^{1}H NMR δ 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}C NMR δ 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}P NMR δ 6.7; HRMS (ESI positive) *m/z* calcd for $C_{28}H_{19}NaOP$ ($[M+Na]^+$): 425.1066. Found: 425.1064.

Hept-1-yn-1-yl(phenyl)(2-(4-tolylethynyl)phenyl)phosphine oxide (1d): a pale yellow oil; IR (CH_2Cl_2) 2924, 2852, 2194, 1465, 1200, 538 cm^{-1}; ^{1}H NMR δ 0.81 (t, J = 7.1 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}C NMR δ 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, 131.9, 132.0, 132.0, 133.3, 133.4, 133.6, 133.6, 134.1, 135.5, 138.9; ^{31}P NMR δ 5.9; HRMS (ESI positive) *m/z* calcd for $C_{28}H_{27}NaOP$ ($[M+Na]^+$): 433.1692. Found: 433.1692.

Hept-1-yn-1-yl(2-(4-methoxyphenylethynyl)phenyl)(phenyl)phosphine oxide (1e): a pale yellow oil; IR (CH_2Cl_2) 2927, 2193, 1605, 1511, 1251, 1200 cm^{-1}; ^{1}H NMR δ 0.81 (t, J = 7.2 Hz, 3H), 1.19-1.50 (m, 6H), 2.33 (dt, J_d = 3.5 Hz, J_t = 7.2 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}C NMR δ 13.9, 19.9, 19.9, 22.1, 27.3, 27.3, 31.1, 55.4, 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, 131.9, 132.0, 132.0, 132.4, 132.9, 133.1, 133.2, 133.3, 133.3, 133.4, 133.4, 133.5, 134.2, 160.0; ^{31}P NMR δ 6.1; HRMS (ESI positive) *m/z* calcd for $C_{28}H_{27}NaO_2P$ ($[M+Na]^+$): 449.1641. Found: 449.1641.

(2-(4-Chlorophenylethynyl)phenyl)(hept-1-yn-1-yl)(phenyl)phosphine oxide (1f): a yellow oil; IR (CH_2Cl_2) 2928, 2193, 1583, 1491, 1201, 693, 535 cm^{-1}; ^{1}H NMR δ 0.82 (t, J = 7.1 Hz, 3H), 1.17-1.32 (m, 4H), 1.46-1.52 (m, 2H), 2.34 (dt, J_d = 3.5 Hz, J_t = 6.9 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}C NMR δ 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, 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}P NMR δ 6.0; HRMS (ESI positive) *m/z* calcd for $C_{27}H_{24}ClNaOP$ ($[M+Na]^+$): 453.1146. Found: 453.1139.

Hept-1-yn-1-yl(phenyl)(2-(4-phenylphenylethynyl)phenyl)phosphine oxide (1g): a pale yellow oil; IR (CH_2Cl_2) 2928, 2193, 1488, 1200, 764, 697, 529 cm^{-1}; ^{1}H NMR δ 0.79 (t, J = 7.4 Hz, 3H), 1.15-1.32 (m, 4H), 1.47-1.53 (m, 2H), 2.36 (dt, J_d = 3.7 Hz, J_t = 7.2 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}C NMR δ 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, 132.0, 132.6, 133.1, 133.3, 133.4, 133.6, 133.6, 133.6, 140.2, 141.4; ^{31}P NMR δ 6.0; HRMS (ESI positive) *m/z* calcd 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_2Cl_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* calcd for $C_{25}H_{23}NaOPS$ ([M+Na]$^+$): 425.1099. Found: 425.1098.

(2-(Dibenzo[*b,d*]thiophen-2-yl-ethynyl)phenyl)(hept-1-yn-1-yl)phenylphosphine oxide (1i): a pale yellow oil; IR (CH_2Cl_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, 132.0, 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* calcd for $C_{33}H_{27}NaOPS$ ([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[14] using *m*CPBA: a pale yellow oil; IR (CH_2Cl_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* calcd for $C_{21}H_{20}NaOS$ ([M+Na]$^+$): 343.1127. Found: 343.1126.

Hept-1-yn-1-yl-bis(2-(4-tolylethynyl)phenyl)phosphine oxide (7): a yellow solid; mp 127 °C; IR (CH_2Cl_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* calcd 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 cycloadduct.

Dimethyl 4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3aa): a pale yellow solid; mp 68 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 128.8, 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; ^{31}P NMR δ 31.8; HRMS (ESI positive) *m/z* calcd for $C_{33}H_{31}NaO_5P$ ($[M+Na]^+$): 561.1801. Found: 561.1801.

Dimethyl 1,4,5-triphenyl-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3ca): a white solid; mp 223 °C; IR (CH_2Cl_2) 2920, 2365, 1740, 1238, 700, 528 cm^{-1}; ^1H NMR δ 3.41 (s, 3H), 3.49 (s, 3H), 6.43-6.46 (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); ^{13}C 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, 127.9, 128.0, 128.1, 128.2, 128.2, 128.8, 128.8, 128.8, 128.9, 129.0, 129.3, 129.6, 129.7, 129.8, 130.8, 130.8, 130.9, 131.1, 131.2, 131.8, 131.9, 132.4, 133.0, 134.6, 135.7, 135.7, 137.0, 137.7, 154.4, 160.2; ^{31}P NMR δ 31.3; HRMS (ESI positive) *m/z* calcd for $C_{34}H_{25}NaO_5P$ ($[M+Na]^+$): 567.1332. Found: 567.1329.

Dimethyl 4-pentyl-5-phenyl-1-(4-tolyl)-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3da): a pale brown solid; mp 63 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 129.5, 129.6, 129.8, 130.0, 131.0, 131.2, 131.3, 132.3, 132.3, 133.0, 133.9, 133.9, 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; ^{31}P NMR δ 31.7; HRMS (ESI positive) *m/z* calcd for $C_{34}H_{33}NaO_5P$ ($[M+Na]^+$): 575.1958. Found: 575.1956.

Dimethyl 1-(4-methoxyphenyl)-4-pentyl-5-phenyl-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3ea): a white solid; mp 102 °C; IR (CH_2Cl_2) 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* calcd for $C_{34}H_{33}NaO_6P$ ([M+Na]$^+$): 591.1907. Found: 591.1904.

Dimethyl 1-(4-chlorophenyl)-4-pentyl-5-phenyl-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3fa): a pale yellow solid; mp 151 °C; IR (CH_2Cl_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, 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* calcd for $C_{33}H_{30}ClNaO_5P$ ([M+Na]$^+$): 595.1412 . Found: 595.1407.

Dimethyl 4-pentyl-5-phenyl-1-(4-phenylphenyl)-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3ga): a white solid; mp 146 °C; IR (CH_2Cl_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, 140.2, 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* calcd for $C_{39}H_{35}NaO_5P$ ([M+Na]$^+$): 637.2114. Found: 637.2110.

Dimethyl 4-pentyl-5-phenyl-1-thienyl-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3ha): a pale yellow oil; IR (CH_2Cl_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, 127.9, 128.8, 128.8, 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, 141.6, 141.6, 146.8, 146.9, 167.1, 167.2, 167.5; ^{31}P NMR δ 31.7; HRMS (ESI positive) *m/z* calcd for $C_{31}H_{29}NaO_5PS$ ([M+Na]$^+$): 567.1366. Found: 567.1365.

2,3-Bis(hydroxymethyl)-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ab): a colorless solid; mp 178 °C; IR (CH_2Cl_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,

1H), 4.36-4.40 (m, 1H), 4.48-4.50 (m, 1H), 4.71-4.79 (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, J_d = 3.2 Hz, J_t = 7.3 Hz, 1H), 7.30-7.31 (m, 2H), 7.38-7.41 (m, 2H), 7.48-7.55 (m, 5H), 7.64-7.68 (m, 2H); ^{13}C 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, 128.7, 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; ^{31}P NMR δ 33.6; HRMS (ESI positive) *m/z* calcd for $C_{31}H_{31}NaO_3P$ ($[M+Na]^+$): 505.1903. Found: 505.1903.

4-Pentyl-1,5-diphenyl-2,3-dipropyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ac): a white solid; mp 86 °C; IR (CH_2Cl_2) 2924, 2853, 1457, 1204, 706 cm^{-1}; ^{1}H NMR δ 0.63-0.75 (m, 4H), 0.79 (t, *J* = 6.9 Hz, 3H), 1.01-1.18 (m, 8H), 1.31-1.62 (m, 4H), 2.32-2.36 (m, 2H), 2.56 (t, *J* = 8.4 Hz, 2H), 2.68 (dt, J_d = 4.5 Hz, J_t = 12.9 Hz, 1H), 2.96 (dt, J_d = 4.5 Hz, J_t = 12.9 Hz, 1H), 5.99 (dd, *J* = 3.2, 8.1, 1H), 6.99-7.04 (m, 1H), 7.08-7.13 (m, 1H), 7.24-7.27 (m, 1H), 7.31-7.33 (m, 1H), 7.38-7.42 (m, 2H), 7.47-7.55 (m, 5H), 7.68-7.74 (m, 2H); ^{13}C NMR δ 10.9, 14.0, 14.8, 15.0, 22.4, 23.5, 24.5, 24.9, 29.7, 32.3, 32.5, 32.7, 33.4, 48.6, 98.4, 101.8, 106.9, 111.3, 111.5, 115.3, 118.7, 120.0, 124.0, 124.7, 125.9, 127.3, 127.7, 128.3, 128.5, 128.5, 128.6, 128.6, 128.9, 129.2, 129.3, 129.5, 129.7, 131.5, 146.2, 147.3, 148.5; ^{31}P NMR δ 33.0; HRMS (ESI positive) *m/z* calcd for $C_{35}H_{39}NaOP$ ($[M+Na]^+$): 529.2631. Found: 529.2632.

4-Pentyl-1,2,3,5-tetraphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ad): a white solid; mp >300 °C; IR (CH_2Cl_2) 2923, 2359, 1738, 1204, 700, 436 cm^{-1}; ^{1}H NMR δ 0.48-0.57 (m, 4H), 0.72-0.88 (m, 4H), 1.13-1.22 (m, 1H), 2.58 (dt, J_d = 4.5 Hz, J_t = 12.7 Hz, 1H), 2.84 (dt, J_d = 4.5 Hz, J_t = 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); ^{13}C 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, 127.1, 127.1, 127.3, 128.2, 128.4, 128.5, 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, 132.7, 133.9, 134.8, 136.4, 136.4, 138.7, 138.7, 138.9, 139.2, 139.5, 142.4, 142.5, 142.7, 142.8, 144.8, 144.9, 147.6; ^{31}P NMR δ 32.9; HRMS (ESI positive) *m/z* calcd for $C_{41}H_{35}NaOP$ ($[M+Na]^+$): 597.2318. Found: 597.2318.

2,3-Bis(4-methoxyphenyl)-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ae): a white solid; mp 228 °C; IR (CH_2Cl_2) 2925, 2360, 1608, 1514, 1246, 1203, 703 cm^{-1}; ^{1}H 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, J_d = 4.6 Hz, J_t = 12.6 Hz, 1H), 2.82 (dt, J_d = 4.6 Hz, J_t = 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); ^{13}C 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, 128.6, 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 δ 33.0; HRMS (ESI positive) *m/z* calcd for $C_{43}H_{39}NaO_3P$ ($[M+Na]^+$): 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_2Cl_2) 2928, 1489, 1201, 1011, 704, 527 cm^{-1}; ^{1}H NMR δ 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 δ 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, 130.3, 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, 144.9, 146.2, 146.2; ^{31}P NMR δ 32.7; HRMS (ESI positive) *m/z* calcd for $C_{41}H_{33}Br_2NaOP$ ($[M+Na]^+$): 753.0528. Found: 753.0522.

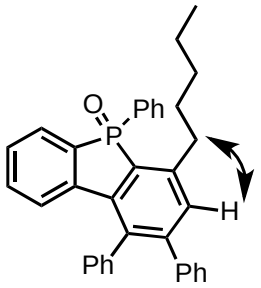
2,3-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ag): a white solid; mp 96 °C; IR (CH_2Cl_2) 2927, 2360, 2189, 1359, 1202, 1144, 417 cm^{-1}; ^{1}H NMR δ 0.44-0.56 (m, 4H), 0.71-0.94 (m, 5H), 1.27 (s, 12H), 1.31 (s, 12H), 2.49-2.55 (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 δ 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 δ 33.0; HRMS (ESI positive) *m/z* calcd for $C_{53}H_{57}B_2NaO_5P$ ($[M+Na]^+$): 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_2Cl_2) 2925, 1738, 1458, 1203, 701, 520 cm^{-1}; ^{1}H NMR δ 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 δ 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, 129.8, 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 δ 32.5; HRMS (ESI positive) *m/z* calcd for

$C_{37}H_{31}NaOPS_2$ ([M+Na]$^+$): 609.1446. Found: 609.1445.

Methyl 4-pentyl-1,2,5-triphenyl-5*H*-dibenzo[*b,d*]phosphole-3-carboxylate 5-oxide (3ai) and methyl 4-pentyl-1,3,5-triphenyl-5*H*-dibenzo[*b,d*]phosphole-2-carboxylate 5-oxide (4ai): a pale yellow solid; mp 131 °C; IR (CH_2Cl_2) 2925, 1733, 1206, 701, 444 cm^{-1}; ^{1}H 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); ^{13}C 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, 128.8, 128.9, 129.0, 129.0, 129.1, 129.5, 129.5, 129.6, 129.7, 129.7, 130.1, 130.1, 130.6, 130.7, 131.4, 131.4, 131.5, 131.5, 131.5, 131.7, 132.1, 131.2, 132.2, 132.6, 132.8, 132.9, 132.9, 133.3, 133.3, 133.4, 133.7, 134.1, 134.5, 135.7, 136.4, 136.9, 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; ^{31}P NMR δ 32.0, 32.5; HRMS (ESI positive) *m/z* calcd for $C_{37}H_{33}NaO_3P$ ([M+Na]$^+$): 579.2060. Found: 579.2059.

4-Pentyl-1,2,5-triphenyl-5*H*-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 (CH_2Cl_2) 2922, 2359, 1739, 1466, 1365, 1204 cm^{-1}; ^{1}H 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); ^{13}C NMR δ 13.9, 22.4, 30.6, 31.7, 33.6, 33.7, 125.4, 125.5, 126.7, 127.5, 127.5, 128.5, 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; ^{31}P NMR δ 31.9; HRMS (ESI positive) *m/z* calcd for $C_{35}H_{31}NaOP$ ([M+Na]$^+$): 521.2005. Found: 521.2007.



3aj

2,3-Bis(methoxycarbonyl)-4-pentyl-1-phenyldibenzo[*b,d*]thiophene-5-oxide (6a): a yellow oil; IR (CH_2Cl_2) 2925, 2853, 1737, 1436, 1038, 702 cm^{-1}; ^{1}H 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); ^{13}C 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 $C_{27}H_{26}NaO_5S$ ([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 (CH_2Cl_2) 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); ^{13}C NMR δ 13.9, 22.1, 30.7, 31.3, 32.1, 125.5, 125.9, 126.7, 126.8, 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, 138.6, 138.9, 142.2, 143.0, 143.1, 145.1, 146.9; HRMS (ESI positive) *m/z* calcd for $C_{35}H_{30}NaOS$ ($[M+Na]^+$): 521.1910. Found: 521.1915.

2,3-Bis(hydroxymethyl)-4-pentyl-1-(4-tolyl)-5-(2-(4-tolylethynyl)phenyl)-5*H*-dibenzo[*b,d*]phosphole 5-oxide (8): a white solid; mp 124 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 125.6, 128.2, 128.3, 128.3, 128.4, 128.8, 128.8, 128.9, 128.9, 129.1, 129.3, 129.8, 130.6, 130.8, 131.4, 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; ^{31}P NMR δ 31.0; HRMS (ESI positive) *m/z* calcd for $C_{41}H_{39}NaO_3P$ ($[M+Na]^+$): 633.2529. Found: 633.2525. $[\alpha]^{28}_D$ -10.4 (c 0.21, $CHCl_3$, 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-5*H*-dibenzo[*b,d*]phosphole-2,3-dicarboxylate 5-oxide (3ia): a white solid; mp 131 °C; IR (CH_2Cl_2) 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, 6H), 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); ^{13}C 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, 128.9, 129.7, 129.7, 129.8, 129.8, 129.9, 130.7, 130.7, 131.2, 131.2, 131.3, 131.3, 131.3, 132.4, 133.2, 133.2, 133.3, 133.9, 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, 145.7, 145.8, 145.8, 167.3, 167.3, 167.4, 167.4, 167.8; ^{31}P NMR δ 31.7; HRMS (ESI positive) *m/z* calcd for $C_{39}H_{33}NaO_5PS$ ($[M+Na]^+$): 667.1679. Found: 667.1678.

1-(Dibenzo[*b,d*]thiophen-2-yl)-4-pentyl-2,3,5-triphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3id): a

white solid; mp 259 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 125.4, 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, 132.1, 132.1, 132.1, 132.1, 132.1, 132.3, 132.3, 132.9, 133.0, 134.0, 134.1, 134.9, 134.9, 135.5, 135.6, 135.6, 135.9, 135.9, 136.0, 136.1, 136.1, 136.1, 136.2, 138.3, 138.4, 138.8, 138.8, 139.1, 139.1, 139.2, 139.3, 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; ^{31}P NMR δ 32.9; HRMS (ESI positive) *m/z* calcd for $C_{47}H_{37}NaOPS$ ($[M+Na]^+$): 703.2195. Found: 703.2190.

2-Dibenzo[*b,d*]thiophen-2-yl-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3ak): a white solid; mp 104 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 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; ^{31}P NMR δ 31.9; HRMS (ESI positive) *m/z* calcd for $C_{41}H_{33}NaOPS$ ($[M+Na]^+$): 627.1882. Found: 627.1879.

1,2-Bis(dibenzo[*b,d*]thiophen-2-yl)ethyne (2l): a pale grey solid; mp 283 °C; IR (CH_2Cl_2) 1739, 1364, 1217, 417 cm^{-1}; ^1H NMR (DMSO-d_6) 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); ^{13}C NMR ($CDCl_3$ with CS_2) 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 $C_{26}H_{15}S_2$ ($[M+H]^+$): 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 (CH_2Cl_2) 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), 7.33 (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); ^{13}C 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 $C_{40}H_{43}S_2$ ($[M+H]^+$): 587.2801. Found: 587.2801.

2,3-Bis(dibenzo[*b,d*]thiophen-2-yl)-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3al): a

pale yellow solid; mp 175 °C; IR (CH_2Cl_2) 2924, 1737, 1216, 1204, 703 cm^{-1}; ^1H NMR δ 0.44-0.55 (m, 4H), 0.65-0.88 (m, 4H), 0.92-1.00 (m, 1H), 2.65-2.78 (m, 1H), 2.84-2.97 (m, 1H), 6.27-6.34 (m, 1H), 6.95-7.05 (m, 1H), 7.07-7.15 (m, 2H), 7.18-7.30 (m, 6H), 7.35-7.39 (m, 10H), 7.63-7.72 (m, 3H), 7.79-7.94 (m, 5H); ^{13}C NMR δ 13.6, 17.0, 21.9, 30.0, 37.6, 121.4, 121.5, 121.8, 122.5, 122.7, 122.9, 122.9, 123.0, 123.3, 123.5, 123.7, 124.1, 124.1, 124.2, 124.4, 124.5, 124.7, 124.8, 125.4, 125.5, 126.4, 126.5, 126.9, 126.9, 127.3, 127.4, 128.6, 128.6, 128.7, 128.7, 128.8, 128.8, 128.8, 128.9, 129.0, 129.2, 129.6, 129.8, 129.8, 130.0, 130.1, 130.2, 131.5, 131.6, 131.7, 131.7, 131.9, 132.0, 132.1, 132.1, 133.2, 134.0, 134.4, 134.8, 134.9, 135.0, 135.2, 135.4, 135.8, 136.9, 137.7, 137.7, 139.3, 139.4, 139.4, 139.7, 142.3, 143.0; ^{31}P NMR δ 32.8; HRMS (ESI positive) *m/z* calcd for $C_{53}H_{39}NaOPS_2$ ($[M+Na]^+$): 809.2072. Found: 809.2070.

2,3-Bis(8-(hept-1-yl)dibenzo[*b,d*]thiophen-2-yl)-4-pentyl-1,5-diphenyl-5*H*-dibenzo[*b,d*]phosphole 5-oxide (3am): a colorless solid; mp 61 °C; IR (CH_2Cl_2) 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); ^{13}C 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, 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; ^{31}P NMR δ 33.1; HRMS (ESI positive) *m/z* calcd for $C_{67}H_{67}NaOPS_2$ ($[M+Na]^+$): 1005.4263. Found: 1005.4260.

Synthesis of 4-Pentyl-1,5-diphenyl-2,3-dipropyl-5*H*-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 (CH_2Cl_2) 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, J_d = 4.4 Hz, J_t = 13.0 Hz, 1H), 3.15 (dt, J_d = 4.4 Hz, J_t = 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); ^{13}C 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, 137.7, 140.5, 141.3, 141.4, 142.3, 142.4, 144.6, 144.7, 145.8, 145.8; ^{31}P 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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