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Aromatic C−H Thioalkylphosphinylation of [2.2]Paracyclophanes via Sulfonium Salts

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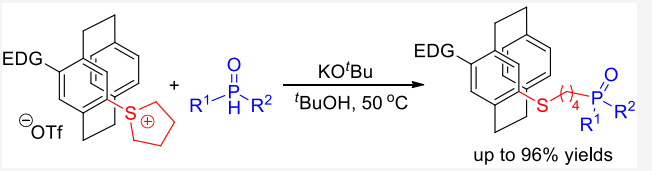
ABSTRACT: Base-enabled aromatic C−H functionalization of [2.2]paracyclophanes was achieved by thioalkylphosphinylation via sulfonium salts. Cross-coupling between [2.2]paracyclophane tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonates and secondary phosphine oxides afforded thioalkylphosphinylated [2.2]-paracyclophane derivatives through selective C(sp^3)−S bond cleavage of the arylsulfonium salts under mild conditions. The protocol features broad substrate scopes, good functional group tolerance from readily available reagents, and decent efficiency in up to 96% yields. The practicability of this method was demonstrated by scale-up preparation of the target products and their transformations to potential P,S-ligands for Suzuki and Sonogashira cross-coupling reactions.



INTRODUCTION

[2.2]Paracyclophane derivatives have attracted much interest in the areas of organic synthesis and materials chemistry over the past decade[1] (Figure 1). Although [2.2]paracyclophane

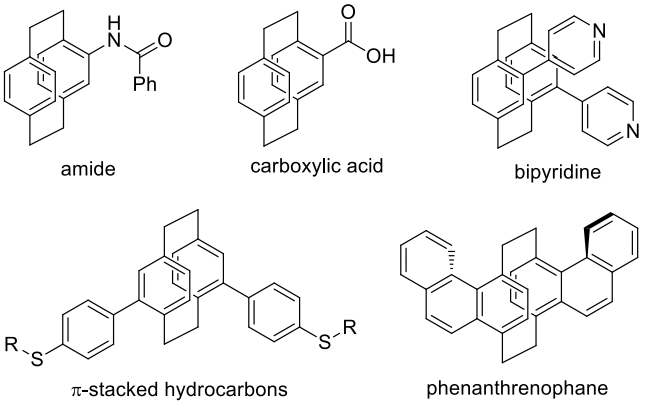


Figure 1. Selected examples of molecules containing a [2.2]-paracyclophane motif.

motif offers diverse modification sites based on its structural feature,[2] it usually remains stable and resistant to alterations by acids, bases, and light. In addition, racemization of [2.2]-paracyclophanes featuring planar chirality often occurs at elevated temperatures.[3] Given the diversity of [2.2]-paracyclophane-based compounds, exploration of their chemical and physical properties is essential and has received more and more attention. Those [2.2]paracyclophanes with planar chirality can serve as ligands for asymmetric synthetic reactions.[4,5] For example, Schafer et al. applied N,O-chelating ligands with a planar chiral [2.2]paracyclophane unit in hydroamination,[4a] and the Bräse group reported planar chiral [2.2]paracyclophane-based dirhodium paddlewheel complex-catalyzed cyclopropanation.[4b]

Heterodonor ligands containing pairs of strong and/or weak donor heteroatoms have been increasingly utilized in organic synthesis due to their distinctive electronic and steric properties.[6] Among the heterodonor ligands, phosphorus−nitrogen ligands have been extensively investigated and applied,[7,8] while phosphorus-thioether ligands have been paid much less attention. Significant electronic disparity exists between phosphorus and sulfur atoms that phosphorus-thioethers have been demonstrated as potential diverse ligands.[9−11] However, [2.2]paracyclophane-based phosphorus-thioether ligands have not yet been reported. In order to functionalize the [2.2]paracyclophane skeleton, [2.2]-paracyclophanes are usually pretreated with liquid bromine or initially functionalized under harsh conditions, followed by further multistep modification processes.[12]

Recently, cyclic sulfonium salts have been shown to have the potential for selective C−S bond cleavage to access diverse organic compounds.[13] In 2021, Huang et al. reported an approach to access ring-opening phosphorus-thioether products from the reaction of arylthianthrenium salts with diarylphosphines via C(sp^2)−P cross-coupling[14] (Scheme 1a). During our continuous investigation of alkenylsulfonium salts, we successfully realized olefinic C−H functionalization

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Scheme 1. C−H Functionalization Strategies via Sulfonium Salts

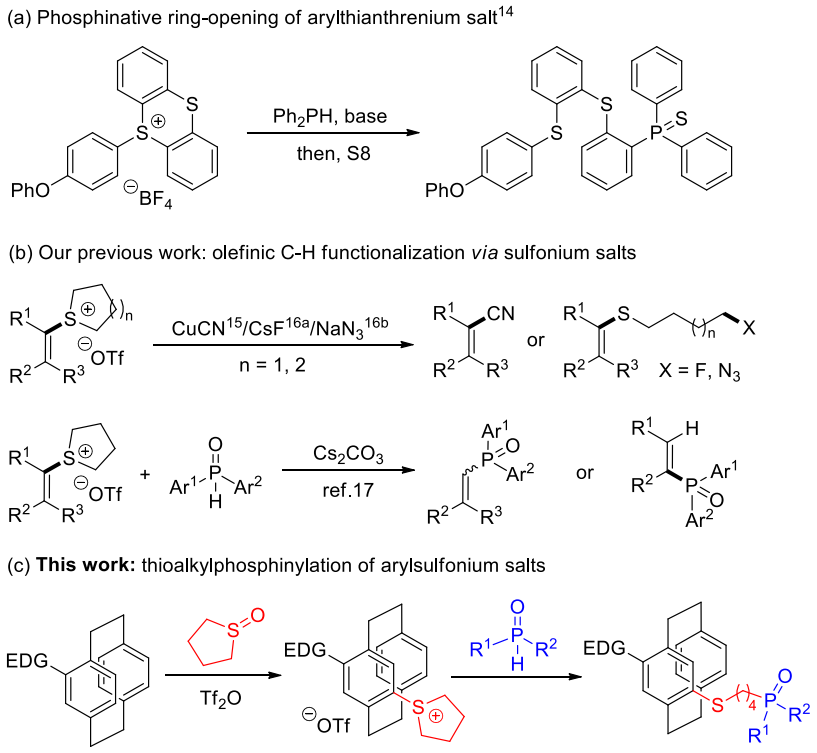
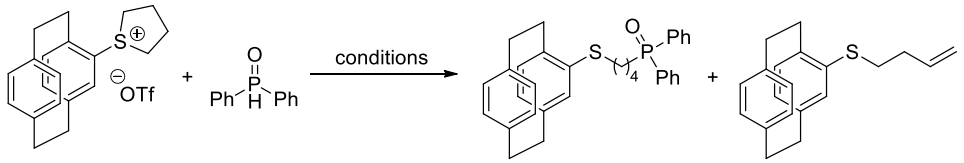


Table 1. Optimization of Reaction Conditions[a]



				yield[b] (%)	
entry	1a/2a	base	solvent	3a	4
1	1:1.1	Cs_2CO_3	EtOAc	61	ND
2	1:1.1	KO^{t}Bu	EtOAc	66	ND
3	1:1.1	KO^{t}Bu	MeCN	38	<5
4	1:1.1	KO^{t}Bu	dioxane	70	<5
5	1:1.1	KO^{t}Bu	^{i}PrOH	74	<5
6	1:1.1	KO^{t}Bu	^{t}BuOH	90	<5
7[c]	1:1.1	KO^{t}Bu	^{t}BuOH	94	<5
8[d]	1:1.1	KO^{t}Bu	^{t}BuOH	94	<5
9[c]	1:1.2	KO^{t}Bu	^{t}BuOH	96	trace
10[d]	1:1.2	KO^{t}Bu	^{t}BuOH	96	trace
11[d,e]	1:1.2	**KO^{t}Bu**	**^{t}BuOH**	**98 (96)**[f]	trace
12	1:1.2		^{t}BuOH	ND	ND
13[d]	1/0	KO^{t}Bu	^{t}BuOH		(98)[f]

[a]Conditions: **1a** (0.20 mmol), **2a** (0.22 mmol), base (0.40 mmol), solvent (2 mL), 28 °C, 12 h, N_2. [b]Determined by ^{1}H NMR analysis by using $MeNO_2$ as the internal standard. [c]40 °C. [d]50 °C. [e]14 h. [f]Isolated yield given in parentheses. ND = Not detected.

through palladium-catalyzed cyanation[15] and thioalkylfluorination,[16a] base-promoted thioalkylazidation[16b] and phosphinylation[17] via selective C(sp^2)−S or C(sp^3)−S bond cleavage of these alkenylsulfonium salts generated from the interrupted Pummerer reaction of the olefinic C−H substrates (Scheme 1b). Furthermore, phosphine oxides, serving as nucleophilic phosphorus-based reagents with favorable reactivity, have been increasingly utilized in organic synthesis.[18] Thus, we reasonably envisioned that [2.2]paracyclophanes might be initially converted into arylsulfonium salts to enhance their reactivities and then undergo further selective transformations. Herein, we disclose a base-promoted selective thioalkylphosphinylation protocol of [2.2]paracyclophane sulfonium salts to

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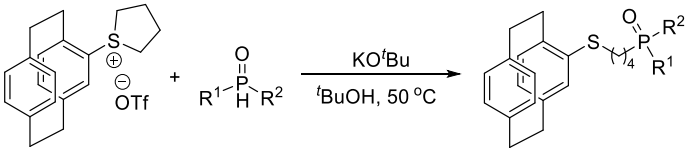
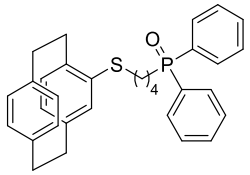
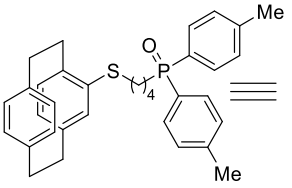
Scheme 2. Scope of Secondary Phosphine Oxides (2)[a]



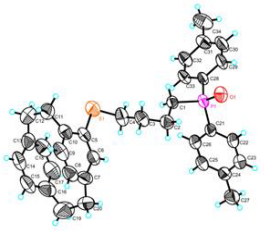
1a **2** **3**



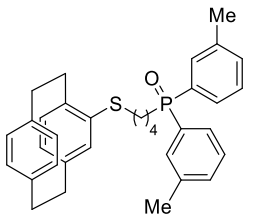
3a, 96%
(1.30 g, 91%)[b]



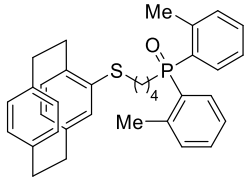
3b, 96%



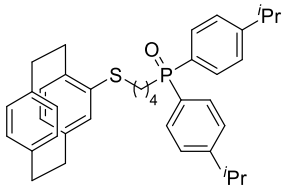
X-ray structure



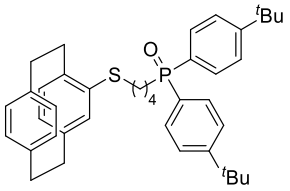
3c, 92%



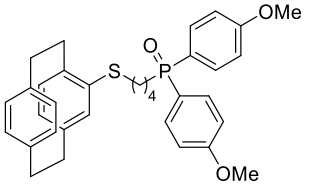
3d, 93%



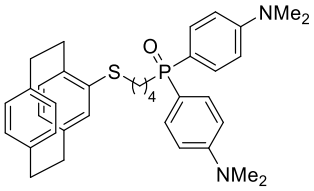
3e, 92%



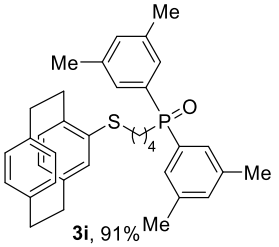
3f, 90%



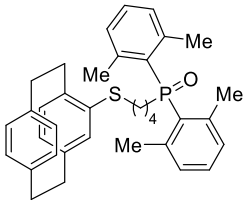
3g, 94%



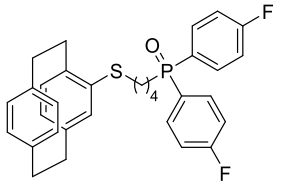
3h, 76%



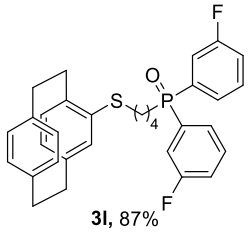
3i, 91%



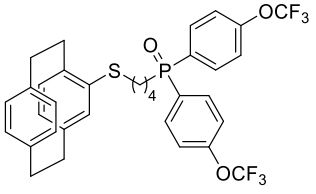
3j, 87%



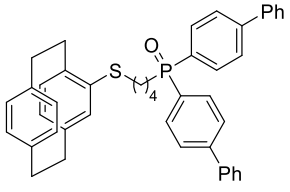
3k, 89%



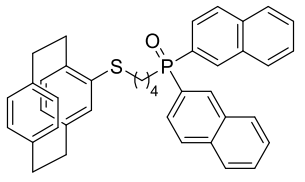
3l, 87%



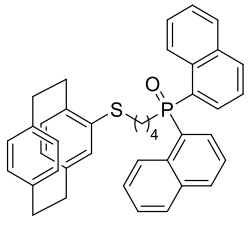
3m, 72%



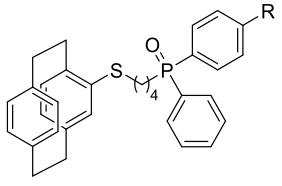
3n, 81%



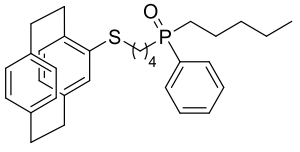
3o, 70%



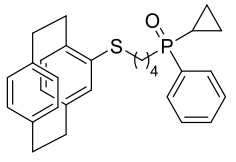
3p, 71%



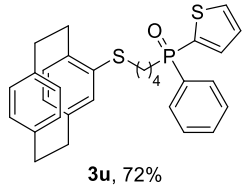
3q, R = Me, 96%
3r, R = F, 90%



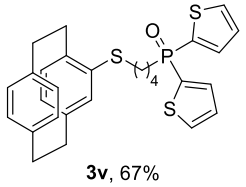
3s, 82%



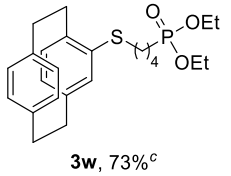
3t, 87%



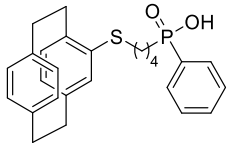
3u, 72%



3v, 67%



3w, 73%[c]



3x, ND

[a]Conditions: **1a** (0.30 mmol), **2** (0.36 mmol), KO^{t}Bu (0.60 mmol), ^{t}BuOH (3 mL), 50 °C, 14 h, N_2. Yields refer to the isolated products. [b]**1a** (3.0 mmol), **2a** (3.6 mmol), KO^{t}Bu (6.0 mmol). [c]K_3PO_4 (0.60 mmol) instead of KO^{t}Bu as the base, THF (3 mL) instead of ^{t}BuOH as the solvent.

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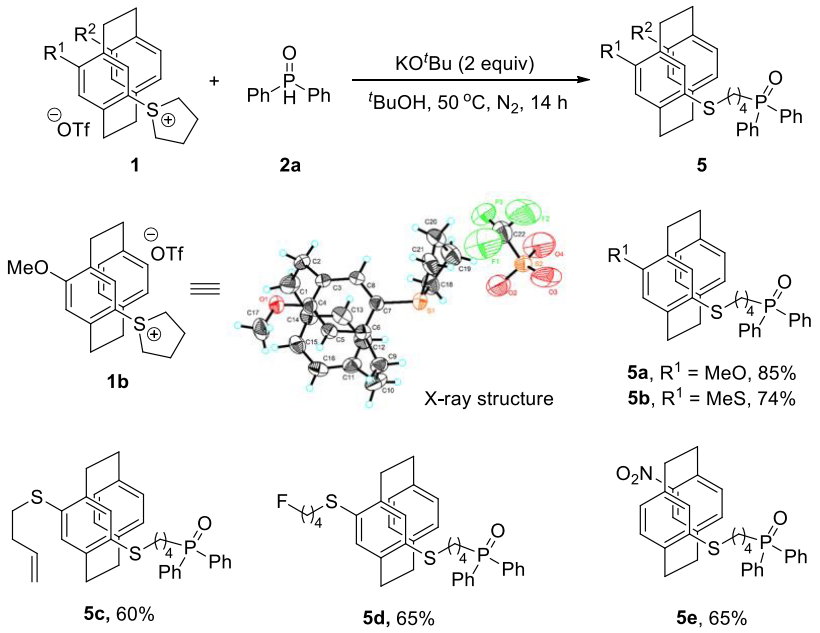
Scheme 3. Scope of [2.2]Paracyclophane Sulfonium Salts (1)[a]



[a]Conditions: **1** (0.30 mmol), **2a** (0.36 mmol), KO^{t}Bu (0.60 mmol), ^{t}BuOH (3 mL), N_2, 50 °C, 14 h. Yields refer to the isolated products.

achieve aromatic C−H functionalization of the [2.2]-paracyclophane skeleton under mild conditions (Scheme 1c).

RESULTS AND DISCUSSION

Arylsulfonium salt 1-([2.2]paracyclophane) tetrahydro-1*H*-thiophen-1-ium trifluoromethanesulfonate (**1a**) was prepared by the interrupted Pummerer reaction of [2.2]paracyclophane, tetrahydrothiophene sulfoxide, and Tf_2O. Initially, the reaction of **1a** and diphenylphosphine oxide (**2a**) was conducted to screen the reaction conditions (Table 1). In the presence of Cs_2CO_3 (2 equiv) as base in EtOAc at ambient temperature, the reaction of **1a** and **2a** in a 1:1.1 molar ratio proceeded to generate the ring-opening phosphinylation product **3a** in 61% yield within 12 h through the selective C(sp^3)−S bond cleavage of **1a** with the C(sp^2)−S bond remaining unchanged (Table 1, entry 1). CsF, KOH, K_3PO_4, NaOMe, and Na_2CO_3 could also act as the base promoters, but potassium *tert*-butoxide behaved more efficiently than them, and *tert*-butyl alcohol turned out to be the suitable reaction medium among the screened solvents such as ethyl acetate, acetonitrile, 1,4-dioxane, isopropanol, etc. (Table 1, entries 2−6, see the SI for details). Elevating the temperature to 40−50 °C enhanced the reaction yield to 94% (Table 1, entries 7 and 8). Increasing the loading of **2a** further improved the reaction efficiency to 96% yield (Table 1, entries 9 and 10). The best result was achieved over a period of 14 h, affording the target product **3a** in 96% isolated yield (Table 1, entry 11). In the absence of a base, the reaction did not occur (Table 1, entry 12). Notably, a ring-opening olefination side product **4** was observed during the reaction (Table 1, entries 3−11), and it was formed in 98% yield by using 2 equiv of base in the absence of nucleophile **2a** (Table 1, entry 13).

Under optimal conditions, the scope of secondary phosphine oxides **2** was explored (Scheme 2). To achieve a broad generality, 50 °C was applied as the reaction temperature. On a 0.3 mmol scale of **1a**, the target product **3a** was also obtained in 96% yield. The gram-scale preparation gave **3a** in 91% yield, demonstrating the good applicability of the synthetic protocol. Electron-donating substituents such as *p*-, *m*-, and *o*-methyls and isopropyl on the aryl moieties of diarylphosphine oxides (**2**) exhibited no obvious negative impact on the reaction efficiency, leading to **3b**-**3e** in 92−96% yields. *p*-*tert*-Butyl and methoxy slightly decreased the yields to 90−94% for **3f** and **3g**, respectively. Unexpectedly, the *p*-dimethylamino group obviously lessened the yield of **3h** (76%), presumably due to both its steric and electronic effects. The diarylphosphine oxides bearing 3,5- and 2,6-dimethyls also efficiently reacted with **1a** to produce the target products **3i** (91%) and **3j** (87%), and electron-withdrawing *p*- and *m*-fluoro groups behaved in a similar manner to facilitate the formation of **3k** (89%) and **3l** (87%). *p*-Trifluoromethoxy deteriorated the yield of **3m** (72%) due to its possible negative steric and electronic effects. The negative steric impact from *p*-phenyl, *p*-(2-naphthyl), and *p*-(1-naphthyl) was observed, furnishing the target products **3n**-**3p** in 70−81%. The unsymmetrical diarylphosphine oxides also efficiently reacted with **1a** to afford products **3q** (96%) from *p*-tolylphenyl-phosphine oxide and **3r** (90%) from *p*-fluorophenylphenyl-phosphine oxide, respectively, and the electronic effect of the substituents was not obvious. Arylalkylphosphine oxides also affected the transformation, and the alkyls differentiated the reaction efficiency to result in **3s** (82%) and **3t** (87%) from *n*-pentyl- and cyclopropyl-based phenylphosphine oxides, respectively. Diethylphosphine oxide was tried as the P(O)−H substrate, but a detectable amount of the target product was not observed from its reaction with **1a** under the reaction conditions. In our previous report on the phosphinylation of alkenylsulfonium salts with secondary phosphine oxides,[17] 1-(2,2-diphenylvinyl)-tetrahydro-1*H*-thiophen-1-ium triflate smoothly reacted with di(cyclohexyl)-phosphine oxide at ambient temperature to form the desired phosphinylated product. These results have suggested that secondary phosphine oxides bearing one or two aryls or two alkyls with a relatively strong electron-donating capability on the phosphorus atom are suitable nucleophilic P(O)−H

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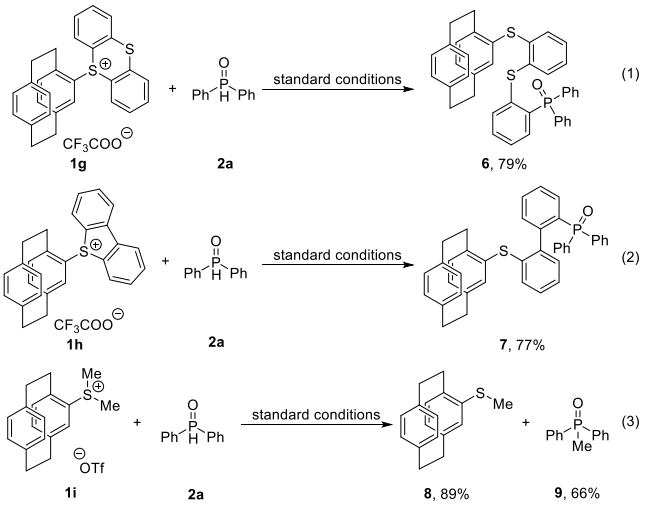
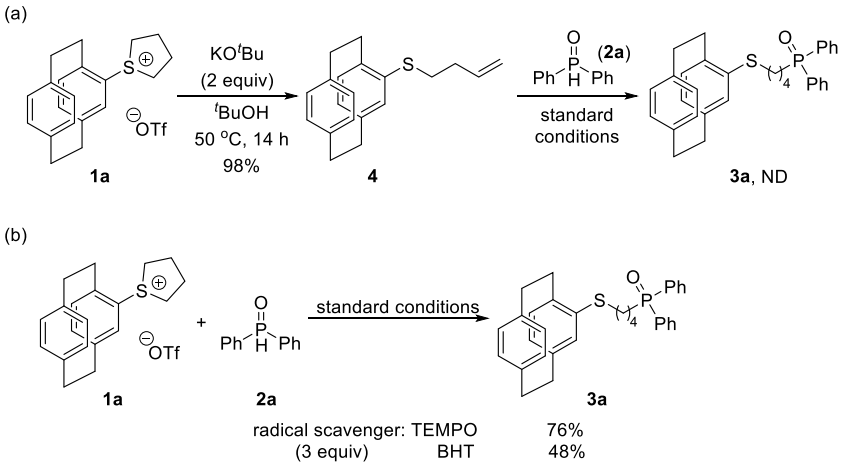
substrates for the phosphinylation process. Arylheteroaryl and di(heteroaryl)phosphine oxides reacted much less efficiently than their diaryl analogs, and treatment of heteroaryl 1-thienyl-based phosphine oxides with **1a** under the standard conditions only gave the target products **3u** (72%) and **3v** (67%) in moderate yields. The H-phosphite substrate, that is, diethyl phosphite, could also undergo the reaction with **1a** under the modified conditions by means of K_3PO_4 as the base and THF as the solvent, yielding **3w** in 73% yield. However, phenylphosphinic acid could not perform the reaction with **1a** under the same conditions to form the desired product **3x**. It is noteworthy that the target products **3** were further identified by the X-ray crystallographic analysis of the molecular structure of phosphorus-thioether compound **3b** (see the Supporting Information for details).

Next, the scope of [2.2]paracyclophane sulfonium salts was investigated (Scheme 3). It should be noted that the interrupted Pummerer reaction of substituted [2.2]-paracyclophanes usually occurred on the relatively electron-rich aryl moiety of the [2.2]paracyclophane skeleton, which was confirmed by the X-ray crystallographic molecular structure of methoxy-substituted [2.2]paracyclophane sulfonium salt **1b** (see the SI for details). For [2.2]paracyclophanes bearing an electron-donating group (EDG) on one of the aryl moieties, the interrupted Pummerer reaction site resided at the *para*-position relative to the electron-donating substituent to form the corresponding arylsulfonium salts. When the [2.2]paracyclophane skeleton bears an electron-withdrawing group (EWG), the interrupted Pummerer reaction preferentially occurs at the *pseudo para*-position of the other aryl moiety. Substituted [2.2]paracyclophane sulfonium salts (**1b**-**1f**) also effectively reacted with diphenylphosphine oxide (**2a**) under the standard conditions. In the case of methoxy and methylthio as the substituents, the target products **5a** (85%) and **5b** (74%) were efficiently obtained, respectively, whereas alkenyl or fluoro-functionalized alkylthio substituents deteriorated the product yields for **5c** (60%) and **5d** (65%). Notably, the electron-withdrawing group nitro-substituted [2.2]-paracyclophane tetrahydro-1*H*-thiophen-1-ium salt underwent the same ring-opening alkylphosphinylation with **2a** to give the desired product **5e** in 65% yield. Efforts were also made to synthesize other [2.2]paracyclophane sulfonium salts bearing an electron-withdrawing group or halogen functionality. In the cases of using [2.2]paracyclophanes substituted by a CO_2Me or bromo group or a *pseudo para*-dibromo functionality on the (di)aryl backbone, the interrupted Pummerer reactions with tetrahydrothiophene sulfoxide and Tf_2O were complicated and no target sulfonium salts could be isolated. With a formyl (CHO) as the substituent on one of the aryl motifs of [2.2]paracyclophane, the interrupted Pummerer reaction formed four kinds of inseparable sulfonium salts which were not successfully applied in the phosphinylation transformation. It should be noted that electron-donating groups on the (di)aryl backbone of [2.2]paracyclophane facilitate the interrupted Pummerer reaction to form the investigated [2.2]paracyclophane sulfonium salts.

Other sulfurizing reagents such as thianthrene sulfoxide (TTO), dibenzothiophene sulfoxide (DBTO), and dimethyl sulfoxide (DMSO) were also used to prepare the corresponding [2.2]paracyclophane sulfonium salts for comparative study. The reaction of arylthianthrenium salt **1g** with diphenylphosphine oxide (**2a**) gave phosphorus-functionalized diarylthioether **6** (79%) via selective C(sp^2)−S bond cleavage of the thianthrene ring under the standard conditions, forming an aromatic C(sp^2)−P bond [eq 1]. A similar reaction occurred for dibenzothiophen-1-ium salt **1h** with **2a** to afford the target product **7** (77%) [eq 2]. NMR characterization revealed the simultaneous presence of both planar and axial chiralities in the product. The observed axial chirality is attributed to restricted



Scheme 4. Control Experiments



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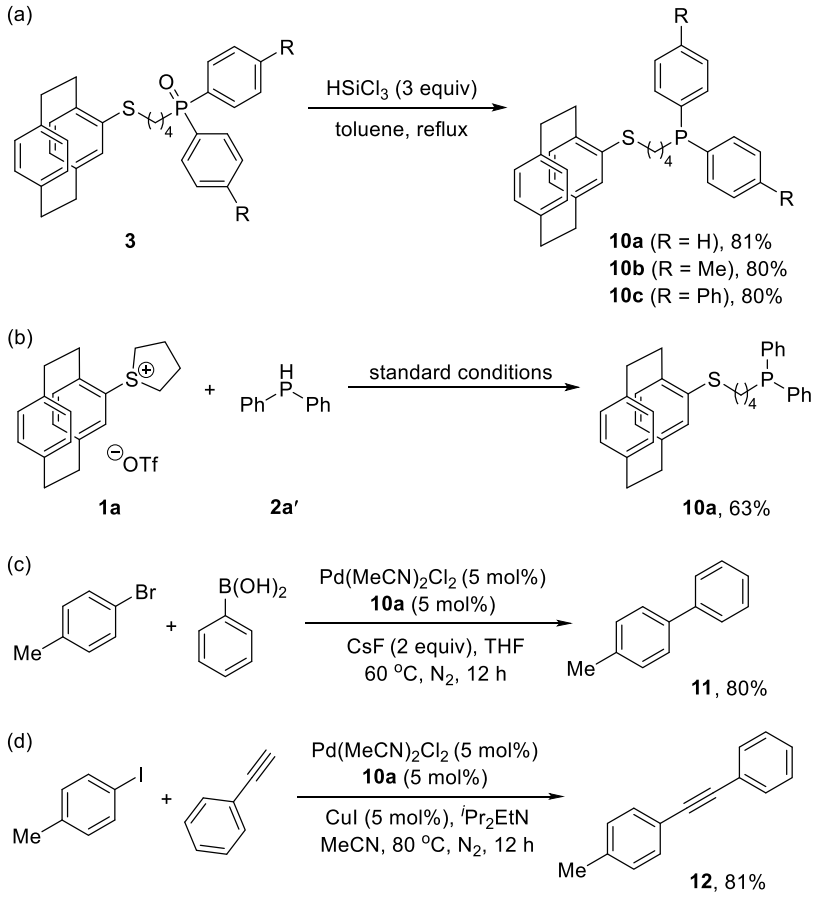
Scheme 5. Derivatization and Application of the Thioalkylphosphinylation Products



rotation of the biphenyl moiety, resulting from steric hindrance between two bulky substituents at the α-positions, which creates a stable chiral axis. It is noteworthy that compound **7** could not be accessed in a decent yield under palladium catalysis.[19] Treatment of aryldimethyl sulfonium salt **1i** with **2a** resulted in the methyl-elimination product **8** (89%) as well as methyldiphenylphosphine oxide **9** (66%) as the methyl transfer product via aliphatic C(sp^3)−S bond cleavage [eq 3].

In order to gain insight into the reaction mechanism, control experiments were performed (Scheme 4). In the absence of the P−H nucleophile and under the basic conditions, [2.2]-paracyclophane sulfonium salt **1a** underwent base-promoted ring-opening olefination to form product **4** in 98% isolated yield (Table 1). Treatment of compound **4** with diphenylphosphine oxide (**2a**) under the standard conditions failed to give the target product **3a**, and no other reaction was observed, revealing that the olefination product **4** is not the intermediate for the investigated transformation (Scheme 4a). It was found that in the presence of a radical scavenger (3 equiv) such as 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), the reaction of sulfonium salt **1a** and **2a** afforded the target product **3a** in 48−76% yields under the standard conditions (Scheme 4b). These radical-trapping reagents could not inhibit the ring-opening thioalkylphosphinylation process, excluding a radical pathway. Thus, we reasonably propose that this reaction is a nucleophilic substitution process of the secondary phosphine oxide anion generated *in situ* by deprotonation of the H−phosphine oxide **2a** in the presence of a base, which proceeds through the C(sp^3)−S bond cleavage of the cycloalkylsulfonium ring of **1a**.[17]

Then, the derivatization and application of the resultant thioalkylphosphinylation products from [2.2]paracyclophanes were carried out (Scheme 5). [2.2]Paracyclophane-based P(V)-thioethers **3** could be reduced to the corresponding thioalkyldiarylphosphine **10a**-**10c** in 80−81% yields with $HSiCl_3$ as the reductant (Scheme 5a). It should be noted that [2.2]paracyclophane sulfonium salt **1a** could also be reacted with diphenylphosphine ($HPPh_2$) to form the corresponding P(III) product **10a** in a moderate yield (63%) (Scheme 5b), but the former two-step phosphinylation/reduction method avoids use of highly toxic P−H reagent and can demonstrate a higher overall efficiency. Compounds **10** are potential bidentate ligands, and their applicability as ligands was exemplified by **10a** in palladium-catalyzed Suzuki-Miyaura cross-coupling reaction of *p*-tolyl bromide and phenylboronic acid, and copper-mediated Sonogashira reaction of *p*-methyliodobenzene with phenylacetylene (Scheme 5c,d), respectively. In both cases, compound **10a** acted as a suitable ligand to promote catalytic transformations. PPh_3 was applied as the ligand in the Suzuki-Miyaura cross-coupling reaction of *p*-tolyl bromide and phenylboronic acid for a comparison study. In the presence of 5 mol % PPh_3 under the same conditions, the reaction showed a 72% yield for the target product **11** (Scheme 5c). This result has demonstrated the higher efficiency of the [2.2]paracyclophane-based thioalkyldiphenylphosphine ligand (**10a**) than the conventional monophosphine ligand.

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In conclusion, base-promoted C−H thioalkylphosphinylation of [2.2]paracyclophanes was achieved via selective C−S bond cleavage of their arylsulfonium salts under mild conditions. The resultant [2.2]paracyclophane-based phosphorus-thioether products could be applied as the potential P,S-ligands for catalytic transformations. This work offers a mild and concise functionalization protocol for [2.2]-paracyclophanes.

EXPERIMENTAL SECTION

General Considerations. The solvents were dried and distilled prior to use by literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a 400 MHz spectrometer, and all chemical shift values refer to $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm). ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra are not calibrated by an internal reference. For reactions that require heating, the heat source was an oil bath. All of the melting points were measured and uncorrected. The X-ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed with UV light (254 nm). Column chromatographic purifications were performed on an SDZF silica gel 160. The starting chemical reagents were purchased from commercial sources and used as received, unless otherwise indicated. Known compounds **2a-c**, **2f**, **2g**, **2l**, **2n**, **2o**, and **2q**,[20] **2d**, **2i**, **2k**, and **2m**,[21] **2e** and **2u**,[22] **2h**,[23] **2j**,[24] **2p**, **2r**, and **2v**,[25] **2s**,[26] **2t**,[27] **9**,[28] **11**,[29] and **12**[30] were prepared by the literature procedures, and their spectroscopic features are in good agreement with those reported in the literature.

*A Typical Procedure for the Preparation of **1a-1f, 1i**. Synthesis of 1-([2.2]Paracyclophane) Tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1a**).* A solution of [2.2]paracyclophane (2.08 g, 10 mmol) and tetrahydrothiophene 1-oxide (1.15 g, 11 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C in a dry ice-acetone bath under a nitrogen atmosphere, and Tf_2O (1.1 equiv) was then added dropwise. The reaction mixture was stirred at −78 °C for 15 min, then allowed to warm up to ambient temperature. The stirring was continued for 24 h at ambient temperature. After [2.2]-paracyclophane was completely consumed by TLC monitoring on silica gel, the resultant mixture was evaporated to remove all the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/methanol = 20:1, v/v), affording **1a** (3.51 g, 79%) as a white solid.

*1-(1,4(1,4)-Dibenzenacyclohexaphane-1^{2}-yl)tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1a**).* Following the general procedure, compound **1a** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 20:1, v/v]. 3.51 g, 79% yield, white solid, m.p.: 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 1.2 Hz, 1H), 6.79 (dd, J = 7.9, 1.3 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.54 (m, 3H), 4.23 (t, 2H), 4.01 (ddd, J = 12.5, 8.2, 7.0 Hz, 1H), 3.64 (ddd, J = 12.8, 9.0, 3.3 Hz, 1H), 3.25 (m, 4H), 3.07 (m, 4H), 2.58 (m, 1H), 2.47 (m, 1H), 2.34 (m, 1H), 2.17 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.8, 141.9, 140.3, 138.8, 138.7, 137.1, 133.8, 133.5, 132.4, 130.9, 130.4, 125.5, 121.05 (q, J = 320.7 Hz).51.4, 43.0, 35.1, 34.8, 34.6, 33.8, 29.4, 28.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.02. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{20}H_{23}S$: 295.1515; found: 295.1514.

*1-(1^{5}-Methoxy-1,4(1,4)-dibenzenacyclohexaphane-1^{2}-yl)-tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1b**).* Following the general procedure, compound **1b** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 50:1, v/v]. 1.15 g, 61% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.72 (dd, J = 7.8, 1.5 Hz, 1H), 6.51 (td, J = 7.8, 1.5 Hz, 2H), 6.42 (dd, J = 8.0, 1.6 Hz, 1H), 5.79 (s, 1H), 4.20 (m, 1H), 4.04 (m, 1H), 3.84 (m, 1H), 3.72 (s, 3H), 3.57 (m, 1H), 3.31 (t, 1H), 3.15 (m, 3H), 3.00 (m, 2H), 2.93 (m, 1H), 2.81 (m, 1H), 2.66 (m, 1H), 2.39 (m, 1H), 2.27 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.0, 146.7, 140.4, 137.9, 132.9, 132.5, 131.4, 131.32, 128.9, 121.0 (q, J = 320.7 Hz), 119.6, 114.4, 55.2, 51.7, 44.5, 34.8, 33.4, 33.3, 30.7, 29.4, 28.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.01. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{21}H_{25}OS$: 325.1621; found: 325.1621.

*1-(1^{5}-(Methylthio)-1,4(1,4)-dibenzenacyclohexaphane-1^{2}-yl)-tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1c**).* Following the general procedure, compound **1c** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 50:1, v/v]. 735 mg, 30% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, J = 7.9, 1.5 Hz, 1H), 6.71 (s, 1H), 6.59 (dd, J = 8.0, 1.5 Hz, 1H), 6.49 (dd, J = 8.0, 1.7 Hz, 1H), 6.36 (dd, J = 7.9, 1.7 Hz, 1H), 6.04 (s, 1H), 4.15 (m, 2H), 3.86 (m, 1H), 3.55 (m, 1H), 3.18 (m, 5H), 2.97 (m, 3H), 2.61 (m, 1H), 2.37 (m, 1H), 2.31 (s, 3H), 2.25 (m, 1H), 2.17 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.0, 143.2, 140.9, 139.5, 138.2, 132.9, 131.1, 131.0, 130.9, 130.7, 127.8, 120.9 (q, J = 320.9 Hz), 119.3, 51.6, 43.8, 34.7, 33.2, 32.9, 32.2, 29.3, 28.3, 14.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.02. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{21}H_{25}S_2$: 341.1392; found: 341.1396.

*1-(1^{5}-(But-3-en-1-ylthio)-1,4(1,4)-dibenzenacyclohexaphane-1^{2}-yl)tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1d**).* Following the general procedure, compound **1d** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 50:1, v/v]. 587 mg, 37% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 7.5 Hz, 1H), 6.73 (s, 1H), 6.59 (dd, J = 31.1, 7.3 Hz, 2H), 6.39 (d, J = 7.4 Hz, 1H), 6.15 (s, 1H), 5.84 (m, 1H), 5.12 (m, 2H), 4.20 (m, 2H), 3.93 (m, 1H), 3.60 (m, 1H), 3.43 (m, 1H), 3.24 (m, 5H), 3.00 (m, 3H), 2.85 (m, 2H), 2.63 (m, 1H), 2.42(m, 2H), 2.32 and 2.20 (m each, 1:1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.1, 143.1, 141.8, 139.7, 138.3, 135.6, 132.9, 132.5, 131.4, 131.2, 130.8, 128.2, 120.9 (q, J = 318.6 Hz), 120.0, 117.0, 51.7, 43.8, 34.7, 33.5, 33.2, 32.5, 32.4, 31.0, 29.4, 28.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.00. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{24}H_{29}S_2$: 381.1705; found: 381.1708.

*1-(1^{5}-((4-Fluorobutyl)thio)-1,4(1,4)-dibenzenacyclohexaphane-1^{2}-yl)tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1e**).* Following the general procedure, compound **1e** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 50:1, v/v]. 776 mg, 47% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, J = 7.9, 1.5 Hz, 1H), 6.73 (s, 1H), 6.62 (dd, J = 7.9, 1.5 Hz, 1H), 6.54 (dd, J = 8.0, 1.6 Hz, 1H), 6.40 (dd, J = 7.9, 1.6 Hz, 1H), 6.17 (s, 1H), 4.53 (t, 1H), 4.41 (t, 1H), 4.19 (m, 2H), 3.92 (m, 1H), 3.58 (m, 1H), 3.28 (m, 1H), 3.18 (m, 4H), 3.00 (m, 3H), 2.84 (m, 2H), 2.63 (m, 1H), 2.42 (m, 2H), 2.32 (m, 1H), 2.20 (m, 1H), 1.88 and 1.81 (m each, 1:3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.0, 143.1, 141.7, 139.7, 138.4, 132.90, 132.5, 131.5, 131.2, 130.8, 128.2, 121.0 (q, J = 318.9 Hz), 119.9, 84.3, 82.7, 51.7, 43.8, 34.7, 33.4, 33.2, 32.5, 31.1, 29.5 (d, J = 19.9 Hz), 29.4, 28.4, 24.49 (d, J = 4.4 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.00, −218.86. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{24}H_{30}FS_2$: 401.1767; found: 401.1772.

*1-(4^{3}-Nitro-1,4(1,4)-dibenzenacyclohexaphane-1^{2}-yl)tetrahydro-1H-thiophen-1-ium Trifluoromethanesulfonate (**1f**).* Following the general procedure, compound **1f** was obtained by column chromatography on silica gel [eluent: CH_2Cl_2/MeOH = 50:1, v/v]. 617.2 mg, 42% yield, the ratio of different substitution sites is 3.7:1, white solid, m.p.: 152−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.63 (s, 2H), 6.59 (s, 2H), 4.37 (m, 1H), 4.24 (m, 1H), 4.15 (m, 1H), 3.70 (m, 1H), 3.33 (m, 4H), 3.13 (m, 4H), 2.59 (m, 2H), 2.45 (m, 1H), 2.22 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.7, 142.1, 140.2, 139.0, 138.7, 137.3, 133.8, 133.6, 132.5, 131.0, 130.3, 125.7, 51.7, 43.0, 35.2, 35.1, 34.7, 34.0, 29.5, 28.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ −78.14. HRMS (ESI-TOF) m/z: [M-OTf]$^{+}$ calcd for $C_{20}H_{22}NO_2S$: 340.1366; found: 340.1367.

*1,4(1,4)-Dibenzenacyclohexaphane-1^{2}-yldimethylsulfonium Trifluoromethanesulfonate (**1i**).* Following the general procedure, compound **1i** was obtained by column chromatography on silica gel [eluent: DCM/MeOH = 20:1 v/v]. 605 mg, 24% yield, white solid, m.p.: 138−139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 1.1 Hz, 1H), 6.79 (dd, J = 7.9, 1.3 Hz, 1H), 6.66 (d, J = 7.9 Hz, 1H), 6.56 (s, 2H), 6.46 (q, J = 8.0 Hz, 2H), 3.50 (m, 1H), 3.44 (s, 3H), 3.16

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(m, 7H), 2.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 141.5, 140.2, 139.2, 138.8, 137.0, 133.63, 133.56, 132.3, 130.9, 130.0, 124.1, 120.9 (q, J = 320.4 Hz), 35.1, 34.8, 34.8, 33.2, 31.7, 24.2. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −78.06. HRMS (ESI-TOF) m/z: $[M\text{-}OTf]^+$ calcd for $C_{18}H_{21}S$: 269.1358; found: 269.1357.

*A Typical Procedure for the Preparation of **1g** and **1h**. Synthesis of 5-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-yl)-5H-thianthren-5-ium 2,2,2-Trifluoroacetate (**1g**).* A solution of [2.2]paracyclophane (2.08 g, 10 mmol) and thianthrene 5-oxide (11 mmol) in CH_2Cl_2 (20 mL) was cooled to −78 °C in dry ice-acetone bath under nitrogen atmosphere, and $(CF_3CO)_2O$ (1.1 equiv) was then added dropwise. The reaction mixture was stirred at −78 °C for 15 min and allowed to warm up to ambient temperature. The stirring was continued for 24 h at ambient temperature. After [2.2]paracyclophane was completely consumed by TLC monitoring on silica gel, the resultant mixture was evaporated with all of the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/methanol = 20:1, v/v), affording **1g** (3.41 g, 64%) as a white solid.

*5-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-yl)-5H-thianthren-5-ium 2,2,2-Trifluoroacetate (**1g**).* Following the general procedure, compound **1g** was obtained by column chromatography on silica gel [eluent: DCM/MeOH = 50:1 v/v]. 3.41 g, 64% yield, white solid, m.p.: 236−237 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 6.6 Hz, 2H), 7.84 (m, 3H), 7.58 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 7.8, 1.4 Hz, 1H), 6.56 (d, J = 7.9 Hz, 1H), 6.49 (dd, J = 7.9, 1.4 Hz, 1H), 6.44 (dd, J = 7.9, 1.5 Hz, 1H), 6.06 (dd, 1H), 5.64 (d, J = 1.3 Hz, 1H), 3.77 (m, 2H), 3.20 (m, 1H), 2.97 (m, 3H), 2.85 (m, 1H), 2.72 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9 (q, J = 33.2 Hz), 142.1, 140.8, 139.3, 138.4, 136.6, 135.6, 135.2, 134.1, 133.9, 133.7, 133.2, 132.2, 131.4, 130.8, 130.6, 130.6, 130.3, 129.9, 122.6, 121.1, 117.4 (q, J = 296.1 Hz), 116.4, 34.9, 34.8, 34.4, 33.6. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −74.57. HRMS (ESI-TOF) m/z: $[M\text{-}CF_3COO]^+$ calcd for $C_{28}H_{23}S_2$: 423.1236; found: 423.1238.

*5-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-yl)-5H-dibenzo[b,d]-thiophen-5-ium 2,2,2-Trifluoroacetate (**1h**).* Following the general procedure, compound **1h** was obtained by column chromatography on silica gel [eluent: DCM/MeOH = 20:1 v/v]. 605 mg, 24% yield, white solid, decomposes at 200 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.9 Hz, 1H), 8.23 (d, J = 7.5 Hz, 1H), 8.04 (d, J = 7.7 Hz, 1H), 7.97 (t, 1H), 7.88 (t, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.63 (t, 1H), 7.44 (t, 1H), 6.90 (dd, J = 7.9, 1.2 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.66 (d, J = 7.9 Hz, 2H), 6.57 (dd, J = 7.8, 1.4 Hz, 1H), 6.29 (dd, J = 8.0, 1.3 Hz, 1H), 5.96 (s, 1H), 4.08 (ddd, J = 14.1, 10.2, 3.7 Hz, 1H), 3.56 (ddd, 1H), 3.45 (ddd, J = 14.3, 10.7, 3.7 Hz, 1H), 3.22 (ddd, 1H), 3.00 (m, 3H), 2.73 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1 (q, J = 40.0 Hz), 144.6, 143.1, 141.08 (s), 140.2, 139.5, 139.1, 138.4, 137.0, 135.2, 133.7, 133.6, 133.3, 133.0, 132.9, 132.6, 131.7, 131.5, 129.3, 128.2, 127.3, 126.9, 125., 124.8, 124.3, 117.6 (q, J = 286.9 Hz), 35.5, 35.1, 34.9, 33.3. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ −74.55. HRMS (ESI-TOF) m/z: $[M\text{-}CF_3COO]^+$ calcd for $C_{28}H_{23}S$: 391.1515; found: 391.1514.

*A Typical Procedure for the Preparation of Symmetrical **2**. Synthesis of Di-p-Tolylphosphine Oxide (**2b**).* Diethyl phosphonate (0.69 g, 5 mmol) in anhydrous THF (10 mL) was slowly added to the arylmagnesium bromide solution (11 mmol, 2.2 equiv) precooled at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 30 min and then further stirred at ambient temperature for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with ethyl acetate (3 × 20 mL). The organic extract was dried in $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether (60−90 °C)/ethyl acetate: 1:1, v/v) to give the target symmetrical diarylphosphine oxide **2b** (1.84 g, 40%) as a white solid.

*Synthesis of Unsymmetrical Phenyl(p-tolyl)phosphine Oxide (**2q**).* Ethyl phenylphosphinate (0.85 g, 5 mmol) in anhydrous THF (10 mL) was slowly added to the *p*-tolylmagnesium bromide solution (11 mmol, 2.2 equiv) precooled at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 30 min and then further stirred at ambient temperature for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with ethyl acetate (3 × 20 mL). The organic extract was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether (60−90 °C)/ethyl acetate: 1:1, v/v) to give target unsymmetrical diarylphosphine oxide **2q** (0.81 g, 75%) as a white solid.

*A Typical Procedure for the Synthesis of **3** and **5**. Synthesis of (4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)-diphenylphosphine Oxide (**3a**).* A mixture of **1a** (133 mg, 0.30 mmol), **2a** (73 mg, 0.36 mmol), and KO^{t}Bu (67 mg, 0.60 mmol) in 3 mL of ^{t}BuOH was vigorously stirred at 50 °C for 14 h under nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1, v/v) to afford compound **3a** (95 mg, 96%). In a similar fashion, other compounds of types **3** and **5** were synthesized, respectively.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)-diphenylphosphine Oxide (**3a**).* Following the general procedure, compound **3a** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 95 mg, 96% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.47 (m, 6H), 6.91 (dd, J = 7.8, 1.4 Hz, 1H), 6.53 (dd, J = 7.8, 1.5 Hz, 1H), 6.44 (dd, J = 7.9, 1.3 Hz, 1H), 6.39 (m, 2H), 6.34 (dd, J = 7.8, 1.4 Hz, 1H), 6.29 (s, 1H), 3.44 (m, 1H), 3.16 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.75 (m, 1H), 2.69 (t, 2H), 2.23 (m, 2H), 1.69 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 140.0, 139.5, 139.2, 137.2, 134.7, 134.6, 133.3, 132.91 (d, J = 98.1 Hz), 132.85, 131.9, 131.8 (d, J = 2.4 Hz), 130.82 (d, J = 9.1 Hz), 130.80, 128.8, 128.7 (d, J = 11.7 Hz), 35.4, 35.1, 34.4, 33.8, 33.1, 30.5 (d, J = 14.6 Hz), 29.4 (d, J = 71.7 Hz), 20.9 (d, J = 3.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 32.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{34}OPS$: 497.2062; found: 497.2066.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-p-tolylphosphine Oxide (**3b**).* Following the general procedure, compound **3b** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 151 mg, 96% yield, white solid, m.p.: 191−192 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.29−7.22 (m, 4H), 6.91 (dd, J = 7.8, 1.4 Hz, 1H), 6.52 (dd, J = 7.8, 1.5 Hz, 1H), 6.44 (dd, J = 7.9, 1.3 Hz, 1H), 6.39 (t, 2H), 6.34 (dd, J = 7.8, 1.4 Hz, 1H), 6.24 (s, 1H), 3.44 (m, 1H), 3.17 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.76 (m, 1H), 2.69 (t, 2H), 2.38 (s, 6H), 2.19 (m, 2H), 1.68 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz). δ 142.1 (d, J = 2.0 Hz), 140.3, 139.9, 139.5, 139.2, 137.3, 134.7, 134.4, 133.3, 132.9, 131.9, 130.9 (d, J = 9.4 Hz), 130.7, 129.9 (d, J = 103.7 Hz), 129.4 (d, J = 11.9 Hz), 128.8, 35.4, 35.1, 34.4, 33.8, 33.0, 30.6 (d, J = 14.6 Hz), 29.6 (d, J = 72.1 Hz), 21.6, 21.0 (d, J = 2.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 32.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{38}OPS$: 525.2375; found: 525.2377.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-m-tolylphosphine Oxide (**3c**).* Following the general procedure, compound **3c** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 145 mg, 92% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 11.8 Hz, 2H), 7.45 (m, 2H), 7.33 (m, 4H), 6.91 (dd, J = 7.8, 1.6 Hz, 1H), 6.52 (dd, J = 7.8, 1.7 Hz, 1H), 6.45 (dd, J = 7.9, 1.6 Hz, 1H), 6.41 (m, 2H), 6.34 (dd, J = 7.8, 1.6 Hz, 1H), 6.24 (d, J = 1.3 Hz, 1H), 3.44 (m, 1H), 3.16 (m, 1H), 3.04 (m, 4H), 2.91 (m, 1H), 2.75 (m, 1H), 2.70 (t, 2H), 2.38 (s, 6H), 2.21 (m, 2H), 1.69 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz). δ 140.4, 134.0, 139.5, 139.3, 138.7 (d, J = 11.2 Hz), 137.3, 134.7, 134.5, 133.4, 132.9, 132.6 (d, J = 2.4 Hz), 132.0 131.5 (d, J = 9.8 Hz), 130.8, 128.9 (d, J = 92.4 Hz), 128.82, 128.77 (d, J = 95.4 Hz), 128.7, 128.5, 127.8 (d, J = 8.8 Hz), 35.5, 35.1, 34.4, 33.8, 33.0, 30.6 (d, J = 14.8 Hz), 29.8, 29.4 (d, J = 71.6 Hz), 29.1, 21.6, 21.0 (d, J = 3.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162

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MHz) δ 32.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{38}OPS$: 525.2375; found: 525.2380.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-o-tolylphosphine Oxide (**3d**).* Following the general procedure, compound **3d** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 146 mg, 93% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.39 (t, 2H), 7.27 (t, 2H), 7.19 (d, J = 4.1 Hz, 1H), 7.17 (d, J = 4.2 Hz, 1H), 6.92 (dd, J = 7.8, 1.8 Hz, 1H), 6.52 (dd, J = 7.8, 1.8 Hz, 1H), 6.44 (dd, J = 7.8, 1.8 Hz, 1H), 6.40 (m, 2H), 6.35 (dd, J = 7.8, 1.8 Hz, 1H), 6.25 (d, J = 1.2 Hz, 1H), 3.46 (m, 1H), 3.17 (m, 1H), 3.02 (m, 4H), 2.91 (m, 1H), 2.76 (m, 1H), 2.71 (t, 2H), 2.32 (m, 8H), 1.72 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz). δ 141.4 (d, J = 8.4 Hz), 140.2, 139.8, 139.3, 139.0, 137.1, 134.5 (d, J = 16.8 Hz), 133.2, 132.7, 132.0−131.5 (m), 130.9 (d, J = 1.0 Hz), 130.6, 128.7, 125.6 (d, J = 11.7 Hz), 35.3, 35.0, 34.3, 33.7, 32.91, 30.5 (d, J = 14.7 Hz), 28.6 (d, J = 71.7 Hz) 21.2 (d, J = 4.1 Hz), 20.9 (d, J = 3.1 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 34.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{38}OPS$: 525.2375; found: 525.2377.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(4-isopropylphenyl)-phosphine Oxide (**3e**).* Following the general procedure, compound **3e** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 160 mg, 92% yield, yellow solid, m.p.: 65−66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.30 (dd, J = 8.0, 2.1 Hz, 4H), 6.93 (dd, J = 7.8, 1.7 Hz, 1H), 6.52 (dd, J = 7.8, 1.7 Hz, 1H), 6.44 (dd, J = 7.9, 1.6 Hz, 1H), 6.39 (m, 2H), 6.34 (dd, J = 7.8, 1.7 Hz, 1H), 6.23 (d, J = 0.9 Hz, 1H), 3.43 (m, 1H), 3.15 (m, 1H), 3.03 (m, 4H), 2.92 (m, 3H), 2.75 (m, 1H), 2.70 (t, 2H), 2.19 (m, 2H), 1.70 (m, 4H), 1.25 (s, 6H), 1.23 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz). δ 152.7 (d, J = 2.6 Hz), 140.3, 139.7, 139.4, 139.1, 137.3, 134.6, 134.2, 133.3, 132.8, 131.8, 130.9, 130.8, 130.6, 130.2 (d, J = 99.6 Hz), 128.7, 126.8 (d, J = 11.9 Hz), 35.4, 35.0, 34.3, 34.1, 33.7, 32.9, 30.5 (d, J = 14.8 Hz), 29.6 (d, J = 71.9 Hz), 23.7, 20.9 (d, J = 3.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{38}H_{46}OPS$: 581.3001; found: 581.3004.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(4-(tert-butyl)phenyl)-phosphine Oxide (**3f**).* Following the general procedure, compound **3f** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 164 mg, 90% yield, white solid, m.p.: 76−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 9.8, 8.6 Hz, 4H), 7.47 (dd, J = 8.2, 2.0 Hz, 4H), 6.92 (dd, J = 7.8, 1.8 Hz, 1H), 6.52 (dd, J = 7.8, 1.8 Hz, 1H), 6.45 (dd, J = 7.9, 1.8 Hz, 1H), 6.40 (m, 2H), 6.34 (dd, J = 7.8, 1.8 Hz, 1H), 6.24 (d, J = 1.2 Hz, 1H), 3.44 (m, 1H), 3.16 (m, 1H), 3.08 (m, 1H), 3.02 (m, 3H), 2.92 (m, 1H), 2.76 (m, 1H), 2.70 (t, 2H), 2.20 (m, 2H), 1.70 (m, 4H), 1.32 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz). δ 155.2 (d, J = 2.5 Hz), 140.4, 139.9, 139.5, 139.2, 137.4, 134.7, 134.4, 133.4, 132.9, 131.9, 130.8 (d, J = 9.6 Hz), 130.7, 129.8 (d, J = 100.8 Hz), 128.8, 125.7 (d, J = 11.9 Hz), 35.5, 35.1, 35.1, 34.4, 33.8, 33.0, 31.2, 30.7 (d, J = 14.8 Hz), 29.7 (d, J = 72.0 Hz), 21.0 (d, J = 3.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{40}H_{49}OPSNa$: 631.3134; found: 631.3126.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(4-methoxyphenyl)-phosphine Oxide (**3g**).* Following the general procedure, compound **3g** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 157 mg, 94% yield, white solid, m.p.: 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 4H), 6.88 (dd, J = 7.8, 1.5 Hz, 1H), 6.72 (m, 4H), 6.52 (dd, J = 7.8, 1.7 Hz, 1H), 6.44 (dd, J = 7.8, 1.6 Hz, 1H), 6.38 (m, 2H), 6.30 (dd, J = 7.8, 1.4 Hz, 1H), 6.09 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.34 (m, 1H), 3.12 (m, 1H), 3.01 (m, 4H), 2.88 (m, 1H), 2.69 (m, 1H), 2.39 (m, 2H), 2.05 (m, 2H), 1.46 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz). δ 162.4, 140.3, 139.3, 139.2, 137.5, 134.5, 133.8, 133.3, 133.0, 132.9, 132.8, 131.9, 130.3, 128.6, 122.2 (d, J = 108.0 Hz), 114.3 (d, J = 12.8 Hz), 55.3, 35.4, 35.0, 34.3, 33.6, 32.1, 30.1 (d, J = 16.7 Hz), 29.5 (d, J = 73.9 Hz), 20.7. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 36.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{38}O_3PS$: 557.2274; found: 557.2280.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(4-(dimethylamino)-phenyl)phosphine Oxide (**3h**).* Following the general procedure, compound **3h** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 133 mg, 76% yield, white solid, m.p.: 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 4H), 6.88 (dd, J = 7.8, 1.4 Hz, 1H), 6.50 (m, 5H), 6.42 (dd, J = 7.8, 1.3 Hz, 1H), 6.37 (m, 2H), 6.29 (dd, J = 7.8, 1.4 Hz, 1H), 6.11 (s, 1H), 3.36 (m, 1H), 3.12 (m, 1H), 3.02 (m, 4H), 2.90 (s, 12H), 2.69 (m, 1H), 2.61 (m, 1H), 2.45 (m, 2H), 2.04 (m, 2H), 1.51 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz). δ 152.3 (d, J = 2.0 Hz), 140.3, 139.4, 139.3, 139.2, 137.7, 134.6, 133.8, 133.3, 132.8, 132.4 (d, J = 10.8 Hz), 131.9, 130.3, 128.62, 116.9 (d, J = 112.4 Hz), 111.5 (d, J = 12.5 Hz), 40.0, 35.4, 35.1, 34.3, 33.7, 32.5, 30.4 (d, J = 15.7 Hz), 29.9 (d, J = 74.0 Hz), 21.2 (d, J = 2.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 36.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{44}N_2OPS$: 583.2906; found: 583.2909.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)bis(3,5-dimethylphenyl)-phosphine Oxide (**3i**).* Following the general procedure, compound **3i** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 151 mg, 91% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 12.5 Hz, 4H), 7.13 (s, 2H), 6.95 (dd, J = 7.8, 1.8 Hz, 1H), 6.53 (dd, J = 7.8, 1.8 Hz, 1H), 6.45 (dd, J = 7.8, 1.7 Hz, 1H), 6.40 (m, 2H), 6.35 (dd, J = 7.8, 1.8 Hz, 1H), 6.25 (s, 1H), 3.99 (q, J = 6.5 Hz, 2H), 3.48 (m, 1H), 3.20 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.77 (m, 3H), 2.32 (s, 12H), 1.84 (m, 2H), 1.71 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.4, 139.8, 139.5, 139.3, 138.3 (d, J = 13.8 Hz), 137.4, 134.7, 134.3, 134.0 (d, J = 2.8 Hz), 133.4, 132.9, 132.0, 131.4 (d, J = 133.8 Hz), 130.7, 129.3 (d, J = 10.1 Hz), 128.8, 64.3 (d, J = 6.1 Hz), 35.5, 35.1, 34.4, 33.8, 33.2, 29.9 (d, J = 6.5 Hz), 25.7, 21.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{42}OPS$: 553.2688; found: 553.2686.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)bis(2,6-dimethylphenyl)-phosphine Oxide (**3j**).* Following the general procedure, compound **3j** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 144 mg, 87% yield, white solid, m.p.: 118−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, 2H), 6.99 (dd, J = 7.5, 3.4 Hz, 4H), 6.90 (dd, J = 7.8, 1.7 Hz, 1H), 6.53 (dd, J = 7.8, 1.8 Hz, 1H), 6.45 (dd, J = 7.8, 1.7 Hz, 1H), 6.41 (m, 2H), 6.34 (dd, J = 7.8, 1.7 Hz, 1H), 6.22 (s, 1H), 3.43 (m, 1H), 3.16 (m, 1H), 3.05 (m, 4H), 2.92 (m, 1H), 2.75 (m, 1H), 2.69 (t, 2H), 2.38 (m, 14H), 1.66 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 141.2 (d, J = 2.7 Hz), 141.1 (d, J = 2.6 Hz), 140.3, 139.8, 139.5, 139.2, 137.3, 134.7, 134.3, 133.4, 132.8, 131.9, 130.7 (d, J = 1.7 Hz), 130.7, 130.3 (d, J = 10.4 Hz), 128.7, 35.6 (d, J = 66.0 Hz), 35.4, 35.1, 34.4, 33.8, 33.1, 30.9 (d, J = 16.2 Hz), 23.0 (d, J = 3.1 Hz), 22.1 (d, J = 2.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 41.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{42}OPS$: 553.2688; found: 553.2688.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(4-fluorophenyl)-phosphine Oxide (**3k**).* Following the general procedure, compound **3k** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 142 mg, 89% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 4H), 7.13 (m, 4H), 6.89 (dd, J = 7.8, 1.7 Hz, 1H), 6.50 (dd, J = 7.8, 1.7 Hz, 1H), 6.41 (m, 3H), 6.32 (dd, J = 7.8, 1.7 Hz, 1H), 6.22 (s, 1H), 3.42 (m, 1H), 3.15 (m, 1H), 3.02 (m, 4H), 2.88 (m, 1H), 2.72 (m, 3H), 2.15 (m, 2H), 1.66 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.92 (dd, J = 253.4, 3.2 Hz), 140.3, 139.9, 139.3, 139.1, 137.0, 134.6, 134.6, 133.3−133.0 (m), 132.8, 131.8, 130.8, 128.7, 116.2 (d, J = 12.8 Hz), 116.0 (d, J = 12.8 Hz), 35.3, 35.0, 34.3, 33.7, 32.9, 30.4 (d, J = 14.6 Hz), 29.4 (d, J = 72.7 Hz), 20.6 (d, J = 3.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 31.2. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −106.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{32}H_{32}F_2OPS$: 533.1876; found: 533.1865.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)bis(3-fluorophenyl)-phosphine Oxide (**3l**).* Following the general procedure,

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compound **3l** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 139 mg, 87% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 6H), 7.21 (m, 2H), 6.90 (dd, J = 7.8, 1.8 Hz, 1H), 6.52 (dd, J = 7.8, 1.8 Hz, 1H), 6.42 (m, 3H), 6.34 (dd, J = 7.8, 1.8 Hz, 1H), 6.26 (d, J = 1.1 Hz, 1H), 3.45 (m, 1H), 3.16 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.76 (m, 1H), 2.70 (t, 2H), 2.20 (m, 2H), 1.69 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 162.69 (dd, J = 250.8, 16.2 Hz), 140.4, 140.1, 139.4, 139.2, 137.0, 135.7 (d, J = 3.0 Hz), 135.6 (d, J = 3.1 Hz), 134.8 (d, J = 16.1 Hz), 133.3, 132.8, 131.9, 131.0, 130.9, 130.9, 130.8, 130.7, 128.8, 126.4 (d, J = 1.7 Hz), 126.3 (d, J = 1.6 Hz), 119.3 (d, J = 2.4 Hz), 119.1 (d, J = 2.3 Hz), 117.8 (d, J = 10.1 Hz), 117.6 (d, J = 9.8 Hz), 35.4, 35.0, 34.4, 33.8, 33.1, 30.4 (d, J = 14.8 Hz), 29.1 (d, J = 72.5 Hz), 20.5 (d, J = 3.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 30.5 (t, J = 5.2 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −110.5 (d, J = 3.0 Hz), −110.46 (d, J = 2.9 Hz). HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{32}H_{32}F_2OPS$: 533.1876; found: 533.1870.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)bis(4-(trifluoromethoxy)-phenyl)phosphine Oxide (**3m**).* Following the general procedure, compound **3m** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 144 mg, 72% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.29 (d, J = 7.9 Hz, 4H), 6.91 (dd, J = 7.8, 1.7 Hz, 1H), 6.51 (dd, J = 7.8, 1.8 Hz, 1H), 6.42 (m, 3H), 6.34 (dd, J = 7.8, 1.7 Hz, 1H), 6.24 (d, J = 1.2 Hz, 1H), 3.44 (m, 1H), 3.16 (m, 1H), 3.03 (m, 4H), 2.90 (m, 1H), 2.73 (m, 3H), 2.17 (m, 2H), 1.67 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 151.9, 140.4, 140.0, 139.4, 139.1, 137.0, 134.7 (d, J = 0.9 Hz), 133.3, 132.8, 132.7 (d, J = 10.2 Hz), 131.9, 131.6 (d, J = 3.1 Hz), 130.8, 130.6 (d, J = 3.0 Hz), 128.8, 120.8 (d, J = 12.4 Hz), 120.3 (q, J = 258.9 Hz), 35.3, 35.0, 34.3, 33.7, 32.9, 30.3 (d, J = 14.7 Hz), 29.2 (d, J = 72.6 Hz), 20.5 (d, J = 3.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 41.1. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −57.6. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{34}H_{32}F_6O_3PS$: 665.1708; found: 665.1711.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di([1,1′-biphenyl]-4-yl)-phosphine Oxide (**3n**).* Following the general procedure, compound **3n** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 158 mg, 81% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 4H), 7.72 (m, 4H), 7.61 (d, J = 7.3 Hz, 4H), 7.47 (t, 4H), 7.40 (m, 2H), 6.95 (dd, J = 7.8, 1.6 Hz, 1H), 6.53 (dd, J = 7.8, 1.6 Hz, 1H), 6.43 (m, 3H), 6.36 (dd, J = 7.8, 1.5 Hz, 1H), 6.27 (s, 1H), 3.47 (m, 1H), 3.19 (m, 1H), 3.04 (m, 4H), 2.92 (m, 1H), 2.76 (m, 3H), 2.31 (m, 2H), 1.81 (m, 2H), 1.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 144.6 (d, J = 2.3 Hz), 140.3, 140.0, 139.9, 139.4, 139.2, 137.2, 134.7, 134.6, 133.3, 132.8, 131.9, 131.4 (d, J = 9.5 Hz), 130.8, 129.0, 128.8, 128.2, 127.4 (d, J = 11.8 Hz), 127.3, 35.4, 35.1, 34.4, 33.8, 33.0, 30.6 (d, J = 14.6 Hz), 29.5 (d, J = 71.9 Hz), 20.9 (d, J = 3.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{44}H_{42}OPS$: 649.2688; found: 649.2684.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-(naphthalen-2-yl)-phosphine Oxide (**3o**).* Following the general procedure, compound **3o** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 126 mg, 70% yield, white solid, m.p.: 145−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.40 (s, 1H), 7.90 (m, 7H), 7.68 (t, 2H), 7.58 (m, 4H), 6.89 (dd, J = 7.8, 1.8 Hz, 1H), 6.51 (dd, J = 7.8, 1.8 Hz, 1H), 6.43 (dd, J = 7.8, 1.7 Hz, 1H), 6.39 (m, 2H), 6.32 (dd, J = 7.8, 1.8 Hz, 1H), 6.22 (d, J = 1.3 Hz, 1H), 3.41 (m, 1H), 3.13 (m, 1H), 3.00 (m, 4H), 2.88 (m, 1H), 2.71 (m, 3H), 2.42 (m, 2H), 1.80 (m, 2H), 1.70 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.1, 139.5, 139.2, 137.2, 134.8 (d, J = 1.3 Hz), 134.7, 134.7, 133.4, 133.0 (d, J = 1.2 Hz), 132.9, 132.7 (d, J = 12.5 Hz), 132.0, 130.8, 129.0, 128.9, 128.7 (d, J = 11.5 Hz), 128.5 (d, J = 6.5 Hz), 128.3, 128.0, 127.1, 125.8 (d, J = 1.8 Hz), 125.7 (d, J = 1.5 Hz), 35.5, 35.1, 34.4, 33.8, 33.1, 30.6 (d, J = 14.6 Hz), 29.3 (d, J = 71.7 Hz), 21.0 (d, J = 3.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.7. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{40}H_{38}OPS$: 597.2375; found: 597.2371.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-(naphthalen-1-yl)-phosphine Oxide (**3p**).* Following the general procedure, compound **3p** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 127 mg, 71% yield, white solid, m.p.: 151−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 7.91 (m, 4H), 7.47 (m, 6H), 6.92 (dd, J = 7.8, 1.7 Hz, 1H), 6.53 (dd, J = 7.8, 1.8 Hz, 1H), 6.43 (m, 3H), 6.34 (dd, J = 7.8, 1.8 Hz, 1H), 6.22 (d, J = 1.2 Hz, 1H), 3.42 (m, 1H), 3.16 (m, 1H), 3.03 (m, 4H), 2.90 (m, 1H), 2.69 (m, 5H), 1.84 (m, 2H), 1.68 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.3, 139.9, 139.4, 139.1, 137.21, 134.6, 134.4, 134.0 (d, J = 8.8 Hz), 133.5 (d, J = 8.1 Hz), 133.3, 133.1 (d, J = 2.7 Hz), 132.8, 131.90, 131.85, 131.8 (d, J = 4.6 Hz), 130.7, 130.1 (d, J = 3.5 Hz), 129.2 (d, J = 3.5 Hz), 129.1, 128.8, 127.4, 126.6 (d, J = 5.0 Hz), 126.5, 124.6 (d, J = 13.4 Hz), 35.4, 35.1, 34.4, 33.8, 32.9, 30.5 (d, J = 15.2 Hz), 30.3 (d, J = 72.0 Hz), 21.4 (d, J = 3.3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 36.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{40}H_{38}OPS$: 597.2375; found: 597.2378.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)(phenyl)-(p-tolyl)-phosphine Oxide (**3q**).* Following the general procedure, compound **3q** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 147 mg, 96% yield, yellow solid, m.p.: 139−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.46 (m, 3H), 7.27 (m, 2H), 6.91 (dd, J = 7.8, 1.7 Hz, 1H), 6.52 (dd, J = 7.8, 1.8 Hz, 1H), 6.44 (dd, J = 7.9, 1.7 Hz, 1H), 6.41 (m, 2H), 6.34 (dd, J = 7.8, 1.8 Hz, 1H), 6.23 (s, 1H), 3.43 (m, 1H), 3.15 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.76 (m, 1H), 2.69 (t, 2H), 2.39 (s, 3H), 2.20 (m, 2H), 1.69 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 142.3 (d, J = 2.7 Hz), 140.4, 140.0, 139.5, 139.2, 137.3, 134.6 (d, J = 17.3 Hz), 133.4, 133.3 (d, J = 96.3 Hz), 132.9, 132.0, 131.7 (d, J = 2.6 Hz), 131.0, 130.9, 130.8, 129.6 (d, J = 100.0 Hz), 129.5 (d, J = 11.8 Hz), 128.8 (d, J = 4.9 Hz), 128.7, 35.5, 35.1, 34.4, 33.8, 33.1, 30.6 (d, J = 14.8 Hz), 29.5 (d, J = 71.9 Hz), 21.7, 21.0 (d, J = 3.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, 23 °C) δ 32.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{33}H_{36}OPS$: 511.2219; found: 511.2215.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)(4-fluorophenyl)(phenyl)-phosphine Oxide (**3r**).* Following the general procedure, compound **3r** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 139 mg, 90% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.47 (m, 3H), 7.13 (m, 2H), 6.91 (dd, J = 7.8, 1.6 Hz, 1H), 6.52 (dd, J = 7.8, 1.7 Hz, 1H), 6.42 (m, 3H), 6.34 (dd, J = 7.8, 1.6 Hz, 1H), 6.23 (s, 1H), 3.44 (m, 1H), 3.16 (m, 1H), 3.03 (m, 4H), 2.90 (m, 1H), 2.73 (m, 3H), 2.19 (m, 2H), 1.69 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 164.9 (dd, J = 253.0, 3.0 Hz), 140.3, 139.9, 139.4, 139.1, 137.1, 134.6 (d, J = 10.0 Hz), 133.4, 133.30, 133.25, 133.2, 132.8, 132.2 (d, J = 3.1 Hz), 131.91, 131.87, 130.8, 130.6, 129.4 (t, J = 3.3 Hz), 128.8, 128.7 (d, J = 4.1 Hz), 128.4 (t, J = 3.5 Hz), 116.2 (d, J = 12.8 Hz), 115.9 (d, J = 12.5 Hz), 35.4, 35.0, 34.3, 33.7, 33.0, 30.4 (d, J = 14.6 Hz), 29.4 (d, J = 72.3 Hz), 20.7 (d, J = 3.6 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 31.7. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −107.0. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{32}H_{33}FOPS$: 515.1968; found: 515.1971.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)(pentyl)-(phenyl)-phosphine Oxide (**3s**).* Following the general procedure, compound **3s** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 121 mg, 82% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.47 (m, 3H), 6.90 (dt, J = 7.8, 2.0 Hz, 1H), 6.51 (dd, J = 7.8, 1.6 Hz, 1H), 6.40 (m, 3H), 6.32 (dt, J = 7.8, 1.9 Hz, 1H), 6.22 (dd, 1H), 3.42 (m, 1H), 3.15 (m, 1H), 3.02 (m, 4H), 2.89 (m, 1H), 2.66 (m, 3H), 1.91 (m, 2H), 1.77 (m, 3H), 1.56 (m, 4H), 1.40 (m, 1H), 1.28 (m, 4H), 0.82 (t, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.3 (d, J = 2.0 Hz), 139.8, 139.4, 139.1, 137.2 (d, J = 2.5 Hz), 134.6, 134.4 (d, J = 3.6 Hz), 133.3, 132.8, 131.8, 131.5 (d, J = 2.7

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Hz), 130.7 (d, J = 2.2 Hz), 130.4 (d, J = 8.8 Hz), 128.7, 128.6, 35.4, 35.0, 34.3, 33.7, 33.1 (d, J = 14.2 Hz), 32.9 (d, J = 2.4 Hz), 30.5 (d, J = 14.3 Hz), 29.8 (d, J = 68.5 Hz), 29.5 (d, J = 68.0 Hz), 22.1, 21.1 (d, J = 4.2 Hz), 20.8 (d, J = 2.0 Hz), 13.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 23 °C) δ 40.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{31}H_{40}OPS$: 491.2532; found: 491.2534.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)-(cyclopropyl)(phenyl)-phosphine Oxide (**3t**).* Following the general procedure, compound **3t** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 120 mg, 87% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.48 (m, 3H), 6.92 (dt, J = 7.8, 1.7 Hz, 1H), 6.52 (dd, J = 7.8, 1.7 Hz, 1H), 6.42 (m, 3H), 6.34 (m, 1H), 6.24 (dd, J = 3.8, 1.2 Hz, 1H), 3.45 (m, 1H), 3.18 (m, 1H), 3.04 (m, 4H), 2.92 (m, 1H), 2.74 (m, 3H), 1.93 (m, 2H), 1.67 (m, 1H), 1.66 (m, 3H), 1.03 (m, 1H), 0.83 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 140.3, 139.9, 139.4, 139.2, 137.3, 134.7, 134.4 (d, J = 2.1 Hz), 133.33, 133.27 (d, J = 97.4 Hz), 132.8, 131.9, 131.6 (d, J = 2.3 Hz), 130.7, 130.3 (d, J = 8.8 Hz), 128.7, 128.6 (d, J = 11.2 Hz), 35.4, 35.1, 35.4, 33.7, 33.0, 30.6 (d, J = 14.4 Hz), 30.3 (d, J = 70.1 Hz), 21.0 (d, J = 3.4 Hz), 6.7 (d, J = 99.8 Hz), 2.9 (d, J = 3.8 Hz), 2.0 (d, J = 4.1 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, 23 °C) δ 38.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{29}H_{33}OPSNa$: 483.1882; found: 483.1885.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)(phenyl)-(thiophen-2-yl)-phosphine Oxide (**3u**).* Following the general procedure, compound **3u** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 102 mg, 72% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.67 (m, 1H), 7.49 (m, 4H), 7.16 (m, 1H), 6.91 (dd, J = 7.8, 1.3 Hz, 1H), 6.52 (dd, J = 7.8, 1.6 Hz, 1H), 6.42 (m, 3H), 6.34 (dd, J = 7.8, 1.0 Hz, 1H), 6.24 (s, 1H), 3.44 (m, 1H), 3.17 (m, 1H), 3.04 (m, 4H), 2.91 (m, 1H), 2.73 (m, 3H), 2.24 (m, 2H), 1.72 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 140.3, 139.9, 139.4, 139.1, 137.1, 135.2 (d, J = 9.2 Hz), 134.7, 134.5 (d, J = 2.2 Hz), 133.3, 133.0 (d, J = 4.5 Hz), 132.9 (d, J = 118.5 Hz), 132.8, 132.0 (d, J = 2.6 Hz), 131.9, 130.7 (d, J = 3.1 Hz), 130.6, 128.8, 128.6, 128.4, 128.3, 35.4, 35.1, 34.4, 33.8, 33.0, 31.6 (d, J = 75.4 Hz), 30.4 (d, J = 15.2 Hz), 20.9 (d, J = 3.8 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 27.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{32}OPS_2$: 503.1627; found: 503.1628.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di-(thiophen-2-yl)phosphine Oxide (**3v**).* Following the general procedure, compound **3v** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 102 mg, 67% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H), 7.58 (dd, J = 7.0, 3.4 Hz, 2H), 7.19 (m, 2H), 6.92 (dd, J = 7.8, 1.8 Hz, 1H), 6.52 (dd, J = 7.8, 1.8 Hz, 1H), 6.45 (dd, J = 7.9, 1.8 Hz, 1H), 6.41 (m, 2H), 6.35 (dd, J = 7.8, 1.8 Hz, 1H), 6.25 (s, 1H), 3.46 (m, 1H), 3.17 (m, 1H), 3.03 (m, 4H), 2.92 (m, 1H), 2.75 (m, 3H), 2.25 (m, 2H), 1.80 (m, 2H), 1.67 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 140.4, 140.0, 139.5, 139.2, 137.2, 135.5 (d, J = 9.9 Hz), 134.7, 134.6, 134.0 (d, J = 110.1 Hz), 133.4, 133.3, 132.9, 132.0, 130.8, 128.8, 128.5 (d, J = 13.8 Hz), 35.5, 35.1, 34.4, 33.8, 33.7 (d, J = 79.2 Hz), 33.1, 30.4 (d, J = 15.9 Hz), 21.1 (d, J = 3.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 21.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{30}OPS_3$: 509.1191; found: 509.1188.

*Diethyl (4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)butyl)-phosphonate (**3w**).* Following the general procedure, compound **3w** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 95 mg, 73% yield, white solid, m.p.: 75−76 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, J = 7.8, 1.8 Hz, 1H), 6.53 (dd, J = 7.8, 1.8 Hz, 1H), 6.43 (m, 3H), 6.37 (dd, J = 7.8, 1.8 Hz, 1H), 6.28 (d, J = 0.8 Hz, 1H), 4.07 (m, 4H), 3.50 (m, 1H), 3.21 (m, 1H), 3.06 (m, 4H), 2.93 (m, 1H), 2.77 (m, 3H), 1.69 (m, 6H), 1.31 (t, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 139.4, 139.0, 138.6, 138.3, 136.4, 133.8, 133.5, 132.4, 131.9, 131.0, 129.8, 127.9, 60.6 (d, J = 6.5 Hz), 34.5, 34.1, 33.5, 32.8, 32.2, 29.3 (d, J = 16.9 Hz), 24.4 (d, J = 141.0 Hz), 20.9 (d, J = 5.0 Hz), 15.6 (d, J = 5.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 31.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{34}O_3PS$: 433.1961; found: 433.1967.

*Synthesis of 1,4(1,4)-Dibenzenacyclohexaphane-1^2-yl(but-3-en-1-yl)sulfane (**4**).* A mixture of **1a** (1.78 g, 4 mmol) and KO^{t}Bu (897.7 mg, 8 mmol) in 10 mL of ^{t}BuOH was vigorously stirred at 50 °C for 14 h under nitrogen atmosphere.

After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1, v/v) to give compound **4** (1.15 g, 98%).

*1,4(1,4)-Dibenzenacyclohexaphane-1^2-yl(but-3-en-1-yl)sulfane (**4**).* Following the general procedure, compound **4** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 1.15 g, 98% yield, colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, J = 7.8, 1.8 Hz, 1H), 6.55 (dd, J = 7.8, 1.9 Hz, 1H), 6.48 (dd, J = 7.8, 1.8 Hz, 1H), 6.44 (m, 2H), 6.39 (dd, J = 7.8, 1.8 Hz, 1H), 6.32 (d, J = 1.0 Hz, 1H), 5.86 (m, 1H), 5.07 (m, 2H), 3.53 (m, 1H), 3.24 (m, 1H), 3.07 (m, 4H), 2.95 (m, 1H), 2.80 (m, 3H), 2.34 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.8, 134.5, 133.4, 132.9, 132.0, 130.8, 128.9, 116.2, 35.5, 35.2, 34.5, 33.84, 33.6, 33.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{23}S$: 295.1515; found: 295.1513.

*(((1^5-Methoxy-1,4(1,4)-dibenzenacyclohexaphane-1^2-yl)thio)-methyl)diphenylphosphine Oxide (**5a**).* Following the general procedure, compound **5a** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 134 mg, 85% yield, white solid, m.p.: 128−129 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.47 (m, 6H), 6.72 (m, 2H), 6.42 (dd, J = 7.8, 1.8 Hz, 1H), 6.39 (s, 1H), 6.31 (dd, J = 7.8, 1.7 Hz, 1H), 5.66 (s, 1H), 3.69 (s, 3H), 3.51 (m, 1H), 3.34 (m, 1H), 3.15 (m, 1H), 3.00 (m, 3H), 2.64 (m, 3H), 2.48 (m, 1H), 2.18 (m, 2H), 1.67 (m, 2H), 1.59 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 157.6, 144.4, 140.5, 139.8, 138.9, 133.6, 133.0, 132.6, 131.79, 131.77, 131.5, 130.9, 130.8, 130.7, 128.8, 128.74, 128.67, 127.8, 127.0, 118.2, 54.5, 35.4, 34.5, 34.2, 33.7, 31.2, 30.9 (d, J = 14.7 Hz), 29.4 (d, J = 71.9 Hz), 20.7 (d, J = 3.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 32.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{36}O_2PS$: 527.2168; found: 527.2169.

*(((1^5-(Methylthio)-1,4(1,4)-dibenzenacyclohexaphane-1^2-yl)-thio)methyl)-diphenylphosphine Oxide (**5b**).* Following the general procedure, compound **5b** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 121 mg, 74% yield, yellow viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (m, 4H), 7.46 (m, 6H), 6.99 (dd, J = 7.8, 1.7 Hz, 1H), 6.86 (dd, J = 7.9, 1.8 Hz, 1H), 6.34 (m, 2H), 6.22 (s, 1H), 6.04 (s, 1H), 3.40 (m, 2H), 3.18 (m, 2H), 3.01 (t, 2H), 2.64 (m, 4H), 2.32 (s, 3H), 2.20 (m, 2H), 1.67 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 141.3, 139.1, 139.0, 138.2, 137.7, 137.1, 133.4 (d, J = 8.0 Hz), 132.5, 132.4, 131.9, 131.8, 131.7, 131.7, 130.8 (d, J = 9.3 Hz), 129.7, 128.7 (d, J = 11.6 Hz), 128.6, 34.2, 33.8, 33.6, 33.6, 33.0, 30.6 (d, J = 14.7 Hz), 29.7, 29.0, 20.7 (d, J = 3.6 Hz), 15.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 32.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{33}H_{36}OPS_2$: 543.1940; found: 543.1944.

*(((1^5-(But-3-en-1-ylthio)-1,4(1,4)-dibenzenacyclohexaphane-1^2-yl)thio)methyl)diphenylphosphine Oxide (**5c**).* Following the general procedure, compound **5c** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 106 mg, 60% yield, yellow viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.48 (m, 6H), 6.93 (dd, J = 7.8, 1.8 Hz, 1H), 6.89 (dd, J = 7.8, 1.8 Hz, 1H), 6.35 (m, 2H), 6.23 (s, 1H), 6.19 (s, 1H), 5.83 (m, 1H), 5.06 (m, 2H), 3.41 (m, 2H), 3.17 (m, 2H), 3.02 (m, 2H), 2.78 (m, 2H), 2.64 (m, 4H), 2.32 (m, 2H), 2.23 (m, 2H), 1.69 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 140.6, 140.5, 139.2 (d, J = 5.1 Hz), 136.6, 136.2, 136.0, 135.6, 135.3, 133.0 (d, J = 99.2 Hz), 132.3, 132.2, 131.89, 131.87, 130.9 (d, J = 9.2 Hz), 129.4, 128.8 (d, J = 11.5 Hz), 116.3, 34.2, 34.1, 33.6, 33.5, 33.4, 33.3, 30.6 (d, J = 14.5 Hz), 29.5 (d, J = 71.5 Hz), 20.9 (d, J = 3.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 32.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{40}OPS_2$: 583.2253; found: 583.2251.

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*(4-((1⁵-((4-Fluorobutyl)thio)-1,4(1,4)-dibenzenacyclohexaphane-1²-yl)thio)butyl)diphenylphosphine Oxide (**5d**).* Following the general procedure, compound **5d** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 118 mg, 65% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.47 (m, 6H), 6.92 (dd, J = 7.8, 1.8 Hz, 1H), 6.89 (dd, J = 7.8, 1.8 Hz, 1H), 6.35 (m, 2H), 6.22 (s, 1H), 6.19 (s, 1H), 4.47 (t, 1H), 4.36 (t, 1H), 3.40 (m, 2H), 3.15 (m, 2H), 3.01 (m, 2H), 2.75 (m, 2H), 2.65 (m, 4H), 2.22 (m, 2H), 1.82 (m, 1H), 1.71 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.5, 140.4, 139.1, 136.1, 135.8, 135.4, 135.3, 132.9 (d, J = 98.2 Hz), 132.2 (d, J = 2.2 Hz), 131.78, 131.75, 130.8 (d, J = 9.2 Hz), 129.28, 129.25, 128.7 (d, J = 11.6 Hz), 83.6 (d, J = 165.3 Hz), 34.04, 34.03, 33.46, 33.45, 33.44, 33.3, 30.5 (d, J = 14.7 Hz), 29.5 (d, J = 19.7 Hz), 29.3 (d, J = 71.8 Hz), 25.2 (d, J = 4.6 Hz), 20.8 (d, J = 3.6 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.2. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz) δ −218.4. HRMS (ESI-TOF) m/z: [M + Na]$^+$ calcd for $C_{36}H_{40}FOPS_2Na$: 625.2134; found: 625.2131.

*(4-((4³-Nitro-1,4(1,4)-dibenzenacyclohexaphane-1²-yl)thio)-butyl)diphenylphosphine Oxide (**5e**).* Following the general procedure, compound **5e** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:4 v/v]. 106 mg, 65% yield, yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2H), 7.69 (d, J = 7.7 Hz, 2H), 7.47 (m, 6H), 6.92 (dd, J = 7.8, 1.5 Hz, 1H), 6.51 (dd, J = 7.8, 1.5 Hz, 1H), 6.44 (dd, J = 7.9, 1.4 Hz, 1H), 6.39 (m, 1H), 6.34 (dd, J = 7.8, 1.4 Hz, 1H), 6.22 (s, 1H), 3.43 (m, 1H), 3.15 (m, 1H), 3.03 (m, 4H), 2.91 (m, 1H), 2.72 (m, 3H), 2.21 (m, 2H), 1.68 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.2, 139.7, 139.3, 139.0, 137.1, 134.5, 134.2, 133.2, 132.7, 131.8, 131.70, 131.68, 130.7, 130.6, 130.5, 128.7, 128.58, 128.55, 35.3, 34.9, 34.2, 33.6, 32.8, 30.4 (d, J = 14.9 Hz), 29.2 (d, J = 71.6 Hz), 20.7 (d, J = 3.5 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 32.5. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{32}H_{33}NO_3PS$: 542.1913; found: 542.1915.

*(2-((2-(1,4(1,4)-Dibenzenacyclohexaphane-1²-ylthio)phenyl)-thio)phenyl)diphenylphosphine Oxide (**6**).* Following the general procedure, compound **6** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 149 mg, 79% yield, white solid, m.p.: 236−237 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 4H), 7.51 (m, 7H), 7.37 (t, 1H), 7.21 (t, 1H), 7.06 (m, 2H), 6.94 (m, 2H), 6.72 (dd, J = 7.8, 1.0 Hz, 2H), 6.50 (m, 5H), 6.36 (dd, J = 7.8, 1.2 Hz, 1H), 3.10 (m, 4H), 2.93 (m, 3H), 2.65 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 143.7, 143.3, 142.9 (d, J = 7.0 Hz), 141.0, 139.6, 139.3, 139.2, 135.4, 135.0, 134.6 (d, J = 10.8 Hz), 133.8, 133.2, 133.1, 132.9, 132.8 (d, J = 2.9 Hz), 132.4, 132.4, 132.3, 132.3, 132.2, 131.9, 131.7 (d, J = 3.1 Hz), 130.7, 130.4, 130.0, 129.8 (d, J = 8.8 Hz), 129.0, 128.6 (d, J = 1.8 Hz), 128.4 (d, J = 1.8 Hz), 127.5, 125.9, 125.4 (d, J = 11.7 Hz), 35.4, 349, 34.7, 34.1. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 30.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{40}H_{34}OPS_2$: 625.1783; found: 625.1788.

*(2′-(1,4(1,4)-Dibenzenacyclohexaphane-1²-ylthio)-[1,1′-biphenyl]-2-yl)-diphenylphosphine Oxide (**7**).* Following the general procedure, compound **7** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 137 mg, 77% yield, dr = 64:36, white solid, m.p.: 115−116 °C. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 6H), 7.43 (m, 6H), 7.28 (m, 3H), 6.93 (m, 1H), 6.84 (m, 1H), 6.54 (m, 6H), 6.37 (m, 2H), 3.11 (m, 6H), 3.01−2.66 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.6 (d, J = 8.6 Hz), 142.7, 140.6, 124.40, 35.4, 34.9, 34.8, 34.2. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 27.5. Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 6H), 7.43 (m, 6H), 7.28 (m, 2H), 7.07 (m, 1H), 6.93 (m, 2H), 6.84 (m, 2H), 6.71 (m, 2H), 6.54 (m, 2H), 6.37 (m, 2H), 3.50 (m, 1H), 3.28 (m, 2H), 3.11 (m, 2H), 3.01−2.66 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.3 (d, J = 8.1 Hz), 142.7, 140.7, 139.7, 124.6, 35.4, 34.9, 34.5. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 28.0. The ^{13}C{^{1}H} NMR signals for the phenyl protons for both isomers: δ 139.5, 139.3, 139.2, 139.2, 138.3, 138.0, 137.8 (d, J = 4.0 Hz), 136.5, 136.3, 135.4, 135.2, 134.9, 134.4, 134.2, 134.21, 134.18, 134.1, 134.0, 133.7, 133.5, 133.2, 133.14, 133.09, 133.07, 133.0, 132.9, 132.9, 132.8, 132.74, 132.70, 132.6, 132.5, 132.4, 132.3, 132.23, 132.18, 132.12, 132.1, 132.0, 131.6, 131.51, 131.46 (d, J = 2.7 Hz), 131.4 (d, J = 2.3 Hz), 131.27, 131.25, 131.2, 131.1, 131.0 (d, J = 2.7 Hz), 129.6, 129.5, 128.5, 128.4, 128.3, 128.13, 128.11, 128.08, 128.0, 127.8, 127.5, 127.4, 127.2, 127.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{40}H_{34}OPS$: 593.2062; found: 593.2064.

*1,4(1,4)-Dibenzenacyclohexaphane-1²-yl(methyl)sulfane (**8**).* Following the general procedure, compound **8** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v]. 68.2 mg, 89% yield, white solid, m.p.: 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 7.8 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.46 (d, J = 7.8 Hz, 1H), 6.39 (m, 3H), 6.11 (s, 1H), 3.45 (m, 1H), 3.26 (m, 1H), 3.03 (m, 5H), 2.79 (m, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.5, 139.5, 139.3, 139.1, 137.9, 134.6, 133.6, 132.9, 131.6, 130.6, 129.6, 128.1, 35.5, 35.3, 34.1, 33.4, 15.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{17}H_{19}S$: 255.1201; found: 255.1205.

*Methyldiphenylphosphine Oxide (**9**).*[28] Following the general procedure, compound **9** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1 v/v].

43.1 mg, 66% yield, white solid, m.p.: 112−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.43 (m, 6H), 1.99 (s, 2H), 1.96 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 134.0 (d, J = 101.3 Hz), 131.8 (d, J = 2.8 Hz), 130.5 (d, J = 9.8 Hz), 128.7 (d, J = 11.8 Hz), 16.6 (d, J = 73.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ 30.0.

*A Typical Procedure for the Preparation of Compounds **10**. Synthesis of (4-(1,4(1,4)-Dibenzenacyclohexaphane-12-ylthio)-butyl)diphenylphosphane (**10a**).* A mixture of **3a** (496 mg, 1 mmol), $HSiCl_3$ (406 mg, 3 mmol), and toluene (5 mL) was stirred at 120 °C for 24 h under nitrogen atmosphere, and then all the volatiles evaporated under reduced pressure.

The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60−90 °C)/ethyl acetate = 10:1, v/v), affording **10a** as a white solid (389 mg, 81%).

A mixture of **1a** (133 mg, 0.3 mmol), $HPPh_2$ (67 mg, 0.36 mmol), and KO^{t}Bu (67 mg, 0.6 mmol) in 3 mL of ^{t}BuOH was vigorously stirred at 50 °C for 14 h under nitrogen atmosphere.

After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 10:1, v/v) to afford compound **10a** (85 mg, 63%).

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1²-ylthio)butyl)-diphenylphosphane (**10a**).* Following the general procedure, compound **10a** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 389 mg, 81% yield, colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 4H), 7.35 (m, 6H), 6.98 (dd, J = 7.7, 1.2 Hz, 1H), 6.56 (dd, J = 7.8, 1.3 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 6.43 (m, 2H), 6.39 (dd, J = 8.0, 1.3 Hz, 1H), 6.27 (s, 1H), 3.50 (m, 1H), 3.22 (m, 1H), 3.08 (m, 4H), 2.95 (m, 1H), 2.80 (m, 1H), 2.74 (t, 2H), 2.06 (m, 2H), 1.74 (m, 2H), 1.59 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.3, 139.8, 139.5, 139.2, 138.7 (d, J = 12.5 Hz), 137.6, 134.7, 134.2, 133.4, 132.90, 132.9, 132.7, 131.9, 130.6, 128.8, 128.7, 128.5 (d, J = 6.7 Hz), 35.5, 35.1, 34.4, 33.8, 33.2, 30.8 (d, J = 13.0 Hz), 27.7 (d, J = 11.6 Hz), 25.3 (d, J = 16.4 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz) δ −16.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{32}H_{34}PS$: 481.2113; found: 481.2116.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1²-ylthio)butyl)di-p-tolylphosphane (**10b**).* Following the general procedure, compound **10b** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 203 mg, 80% yield, white solid, m.p.: 186−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, 4H), 7.18 (d, J = 7.6 Hz, 4H), 6.99 (dd, J = 7.8, 1.8 Hz, 1H), 6.57 (dd, J = 7.8, 1.8 Hz, 1H), 6.49 (dd, J = 7.8, 1.7 Hz, 1H), 6.43 (m, 2H), 6.39 (dd, J = 7.8, 1.8 Hz, 1H), 6.28 (d, J = 1.0 Hz, 1H), 3.50 (m, 1H), 3.22 (m, 1H), 3.08 (m, 4H), 2.96 (m, 1H), 2.77 (m, 3H), 2.37 (s, 6H), 2.04 (m, 2H), 1.74 (m, 2H), 1.60 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ 140.3, 139.7, 139.5, 139.2,

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138.6, 137.6, 135.0 (d, J = 9.0 Hz), 134.6, 134.1, 133.4, 132.8, 132.8, 132.8, 132.63, 132.61, 131.9, 130.5, 129.4, 129.3, 128.7, 35.5, 35.1, 34.4, 33.7, 33.1, 30.7 (d, J = 13.1 Hz), 27.8 (d, J = 10.4 Hz), 25.3 (d, J = 16.3 Hz), 21.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ −18.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{34}H_{38}PS$: 509.2426; found: 509.2425.

*(4-(1,4(1,4)-Dibenzenacyclohexaphane-1^2-ylthio)butyl)di([1,1′-biphenyl]-4-yl)-phosphane (**10c**).* Following the general procedure, compound **10c** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 253 mg, 80% yield, yellow viscous liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 8H), 7.61 (t, 4H), 7.52 (t, 4H), 7.43 (t, 2H), 7.07 (dd, J = 7.8, 1.7 Hz, 1H), 6.61 (dd, J = 7.8, 1.8 Hz, 1H), 6.54 (dd, J = 7.8, 1.7 Hz, 1H), 6.48 (m, 3H), 6.36 (d, J = 0.9 Hz, 1H), 3.58 (m, 1H), 3.29 (m, 1H), 3.12 (m, 4H), 3.00 (m, 1H), 2.85 (m, 3H), 2.19 (m, 2H), 1.83 (m, 2H), 1.73 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ 141.4, 140.5, 140.3, 139.7, 139.5, 139.1, 137.5, 137.4, 134.6, 134.2, 133.3, 133.1, 132.8, 131.9, 130.5, 128.9, 128.7, 127.6, 127.2, 127.14, 127.09, 35.4, 35.1, 34.4, 33.7, 33.1, 30.7 (d, J = 13.0 Hz), 27.7 (d, J = 11.5 Hz), 25.3 (d, J = 16.4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ −17.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{44}H_{42}PS$: 633.2739; found: 633.2733.

*Synthesis of 4-Methyl-1,1′-biphenyl (**11**).* A mixture of 1-bromo-4-methylbenzene (34 mg, 0.2 mmol), phenylboronic acid (24 mg, 0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol %), **10a** (4.8 mg, 5 mol %), CsF (61 mg, 0.4 mmol), and THF 2 mL was stirred at 60 °C for 12 h under nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1, v/v) to afford compound **11** (27 mg, 80%).

*4-Methyl-1,1′-biphenyl (**11**).* Following the general procedure, compound **11** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 27 mg, 80% yield, white solid, m.p.: 42.1−43.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.48 (t, 2H), 7.39 (d, J = 7.3 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.1, 127.1, 21.2.

*Synthesis of 1-Methyl-4-(phenylethynyl)benzene (**12**).* A mixture of 1-iodo-4-methylbenzene (44 mg, 0.2 mmol), phenylacetylene (20 mg, 0.2 mmol), $Pd(MeCN)_2Cl_2$ (2.6 mg, 5 mol %), **10a** (4.8 mg, 5 mol %), CuI (1.9 mg, 5 mol %), MeCN (2 mL), and iPr_2EtN (125 ul) was stirred at 80 °C for 12 h under nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1, v/v) to afford compound **12** (31 mg, 81%).

*1-Methyl-4-(phenylethynyl)benzene (**12**).* Following the general procedure, compound **12** was obtained by column chromatography on silica gel [eluent: petroleum ether (60−90 °C)/ethyl acetate = 100:1 v/v]. 31 mg, 81% yield, yellow solid, m.p.: 62.3−63.3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.37 (m, 3H), 7.18 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 131.7, 131.6, 129.2, 128.4, 128.2, 123.6, 120.3, 89.7, 88.9, 21.6.

Gram-Scale Synthesis of 3a. A mixture of **1a** (1.33 g, 3.0 mmol), **2a** (0.73 g, 3.6 mmol), and KO^{t}Bu (0.67 g, 6.0 mmol) in 10 mL of ^{t}BuOH was vigorously stirred at 50 °C for 14 h under nitrogen atmosphere. After the mixture was cooled to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1, v/v) to afford compound **3a** (1.35 g, 91%).

TEMPO or BHT-Trapping Radical Experiments. A mixture of **1a** (133 mg, 0.3 mmol), **2a** (73 mg, 0.36 mmol), KO^{t}Bu (67 mg, 0.60 mmol), and TEMPO or BHT (2,6-di-*tert*-butyl-4-methylphenol) (1.5 mmol) in 3 mL of ^{t}BuOH was stirred at 50 °C for 14 h under an argon atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 1:1, v/v) to afford compound **3a** in 76/48% yields.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.5c01085.

Experimental materials and procedures, analytical data and NMR spectra of compounds, and X-ray crystallographic analysis for **1b** and **3b** (PDF)

Accession Codes

Deposition Numbers 2360629 and 2396526 contain the supporting crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

Nitromethane is an extremely flammable and explosive liquid, which can detonate upon extreme heat. Contact with amines alkali metals and strong reducing agents should be strictly avoided.

The authors declare no competing financial interest.

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