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Doctoral Dissertation

Studies on the Catalytic Synthesis of Heterocycles through Cleavage of Carbon-Heteroatom Bonds

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January 2015

Graduate School of Engineering,
Osaka University

Preface and Acknowledgements

The research described in this thesis was carried out under the direction of Professor Naoto Chatani in the Department of Applied Chemistry at the Faculty of Engineering of Osaka University from April 2009 to March 2015. The thesis is concerned with the catalytic synthesis of heterocycles through the cleavage of carbon-heteroatom bonds.

I would not have been able to complete this thesis without the heartfelt help and support from many people. Here, I wish to express my appreciation to all of those people who I interacted with during my stay with the Chatani group.

First and foremost, I would like to express my sincere gratitude to Professor Naoto Chatani for his helpful guidance and support throughout this work. In addition, I wish to thank him for providing me with the opportunity to study in USA. This experience was incredibly valuable and irreplaceable in my life. I also wish to express my appreciation to Professor Sensuke Ogoshi and Professor Masahiro Miura for the valuable discussions I had with them.

I would like to give my special thanks to Dr. Mamoru Tobisu for his continuous advice and support. Whenever I came up against a brick wall, he encouraged me with his kind words. I deeply appreciate the instructive advice and discussions from Dr. Yoshiya Fukumoto, and Dr. Toshiaki Shimasaki.

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I wish to acknowledge a Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists and a scholarship from the Asahi Glass Company Scholarship Society.

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Suita, Osaka
March 2015

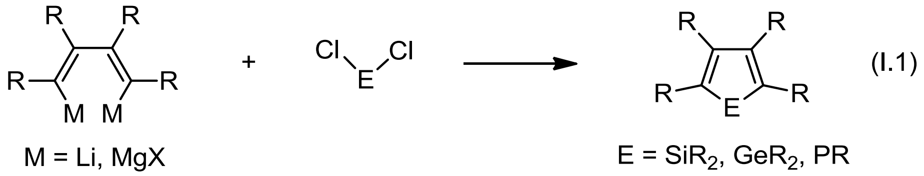
Katsuaki Baba

Contents

General Introduction

Pyrroles and furans, which contain N and O atoms, are widely used in organic materials and pharmaceuticals.[1] Therefore, a number of methods for their synthesis have been reported. On the other hand, the chemistry of heteroles containing Si, Ge, and P has been much less explored compared to pyrroles and furans, although they have recently received considerable attention as promising organic materials because of their characteristic optical and electronic properties.[2]

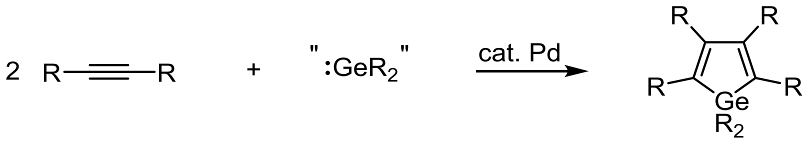
As of this writing, siloles, germoles, and phospholes have been synthesized by using E-X or E-H (E = SiR_2, GeR_2, PR) as heteroatom sources. The most frequently used method for their synthesis involves the nucleophilic substitution of an E-X bond with a stoichiometric amount of an organometallic species such as an organolithium or organomagnesium reagent (eq I.1).[2a,2b,3] However, these methods suffer from low functional group compatibility and the sensitivity of the reagents to air and water.



To overcome these problems, catalytic methods have been being developed for the synthesis of siloles, germoles and phospholes.

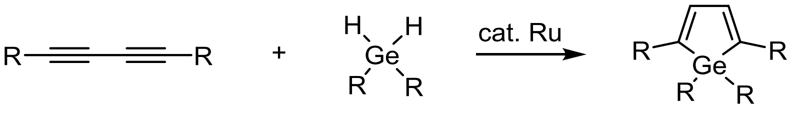
1. Catalytic Synthesis of Germoles

In 1990, the palladium-catalyzed reaction of alkynes with germylenes was reported as the first catalytic synthesis of germoles (eq I.2).[4]

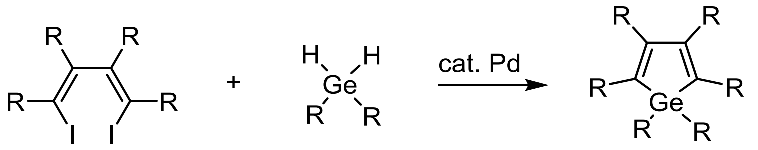


(I.2)

In 2010, Murakami developed the ruthenium-catalyzed reaction of a diyne with a dihydrogermane (eq I.3).[5] Yamanoi and Nishihara also reported on the cross-coupling reaction between iodide and a dihydrogermane (eq I.4).[6]

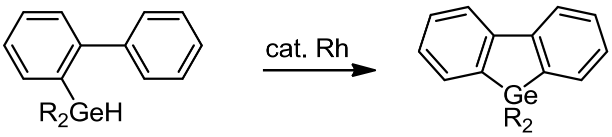


(I.3)



(I.4)

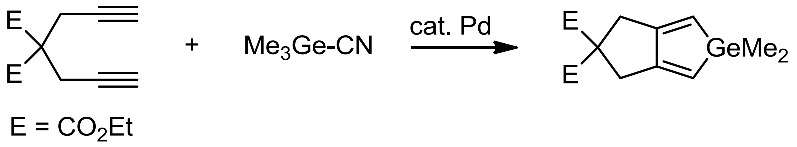
Very recently, Murai and Takai reported on the rhodium-catalyzed dehydrogenative intramolecular reaction of hydrogermanes (eq I.5).[7]



(I.5)

In all of the reactions shown in eqs I.2-I.5, it is necessary to use either a germylene or a hydrogermane, which limits the scope of substrates.

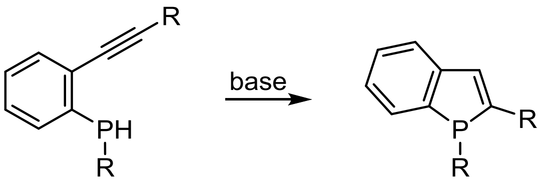
Our group also reported on the palladium-catalyzed synthesis of germoles using a diyne and a germylcyanide (eq I.6).[8] Interestingly, this reaction proceeds through the cleavage of carbon-germanium bonds.



(I.6)

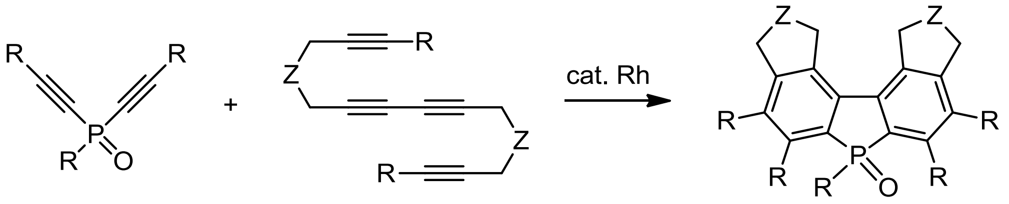
2. Catalytic Synthesis of Phospholes

In previous studies, a number of intramolecular cyclization reactions of alkynes involved the use of a strong base such as *n*-BuLi (eq I.7).[9] However, the use of a strong base can result in low functional group compatibility.



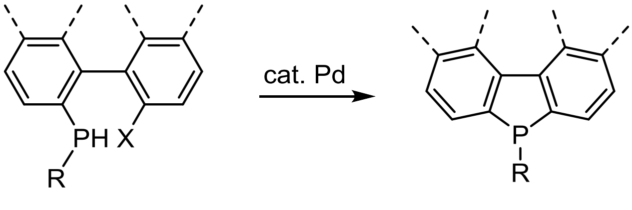
(I.7)

In 2010, Tanaka developed the first catalytic synthesis of phospholes by the [2+2+2] cycloaddition of dialkynylphosphines with polyynes (eq I.8).[10]



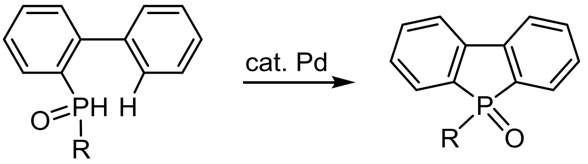
(I.8)

After the Tanaka's report, the intramolecular cross-coupling of aryl halides or their equivalents with hydrophosphines was reported for the synthesis of a phosphole skeleton (eq I.9).[11] However, this method still needs considerable improvement in terms of the degree of functionalization of the starting material and the instability of the hydrophosphine group.



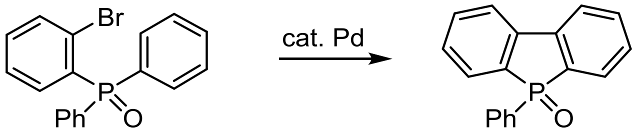
(I.9)

Takai and Kuninobu made notable progress by developing the palladium-catalyzed synthesis of dibenzophosphole oxides by dehydrogenative cyclization of hydrophosphine oxides (eq I.10).[12]



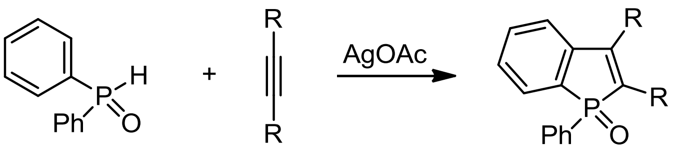
(I.10)

Quite recently, Cui reported on the use of a palladium-catalyzed intramolecular C-H coupling reaction for the synthesis of dibenzophosphole oxides (eq I.11).[13] This method allows the use of a triarylphosphine, which is stable and easy to handle, as a starting material.



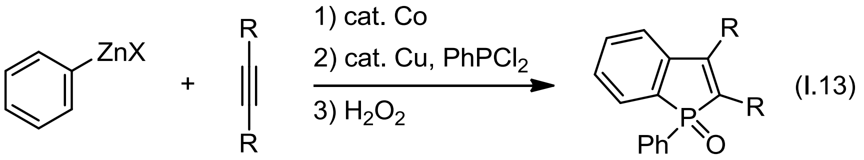
(I.11)

Although no catalytic, some useful methods for the synthesis of phosphole derivatives have recently been developed. Miura, Satoh, and Duan reported on silver-mediated oxidative annulation for the synthesis of benzophosphole oxides (eq I.12).[14]



(I.12)

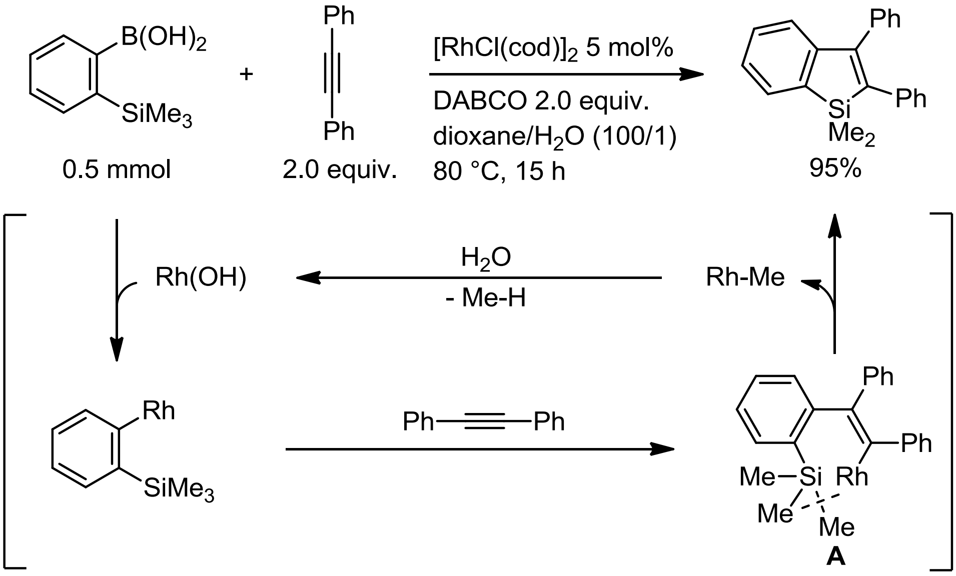
Yoshikai reported on a one-pot cyclization using arylzinc reagents. This reaction proceeds through the migratory arylzincation and a C-P coupling reaction with chlorophosphines (eq I.13).[15]



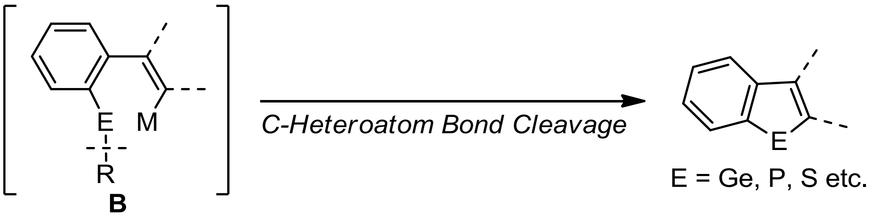
Although catalytic methods for the synthesis of phospholes continue to be developed, avoiding the use of unstable reagent involving a P-H group cannot be completely avoided. Such a problem limits the scope of substrates. Therefore, more general and efficient methodology for the synthesis of heteroles is clearly needed.

Our group recently reported in a catalytic synthesis of benzosiloles (Scheme I.1).[16] In this reaction, a variety of benzosiloles can be synthesized via the use of stable tetraorganosilanes, without the use of chlorosilanes or hydrosilanes. Importantly, the reaction involves the catalytic cleavage of an inert C-Si bond without forming a discrete hypervalent silicate species. The key to such a cleavage of an inactivated bond is considered to be the proximity effect between the rhodium center and C-Si bond in the vinyl rhodium intermediate (Scheme I.1, **A**).

Scheme I.1. Rh-Catalyzed Synthesis of Benzosilole via C-Si Bond Cleavage



Based on the previous report (Scheme I.1), we envisioned that the synthesis of a variety of heteroles through carbon-heteroatom bonds could be accomplished by the generation of key intermediate (eq I.14, **B**). In other words, the proximity effect between the metal and the bond could allow for the carbon-heteroatom bond to be cleaved, this leading to the production of heteroles.



(I.14)

Based on this working hypothesis (eq I.14), the novel catalytic synthesis of germoles and phospholes through the cleavage of carbon-germanium and carbon-phosphorus bond were examined. In this thesis, we focus on methods for the catalytic construction of germole and phosphole frameworks. This thesis consists of the following three chapters.

Chapter 1 discusses the rhodium-catalyzed synthesis of germoles via the activation of carbon-germanium bonds. The reaction involves the activation of C(sp^3)-Ge bonds, which remained unexplored to date.

Chapter 2 deals with the palladium-catalyzed synthesis of benzofuzed phosphacycles via carbon-phosphorus bond cleavage. The method involves C-P bond cleavage, which allows for the use of tertiary phosphines as stable and readily available phosphorus sources.

Chapter 3 is concerned with the palladium-catalyzed direct synthesis of phosphole derivatives from triarylphosphines through the cleavage of carbon-hydrogen and carbon-phosphorus bonds. The reaction involves the catalytic cleavage of two inert bonds, C-H and C-P bonds, in a single catalytic cycle.

Finally, the findings are summarized in the conclusion.

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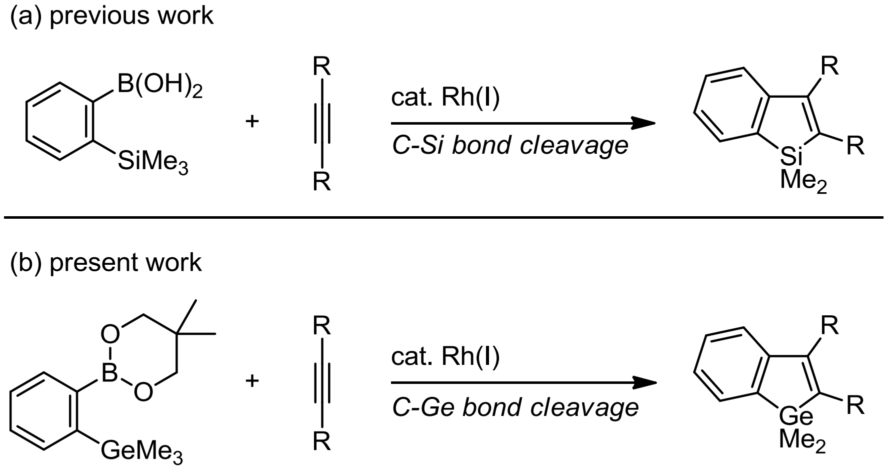
Chapter 1

Rhodium-Catalyzed Synthesis of Germoles via the Activation of Carbon-Germanium Bonds

1.1 Introduction

As described in general introduction, our group recently reported a catalytic reaction that involved the activation of C-Si bonds (Scheme 1.1a).[1] Motivated by the desire to verify the generality of rhodium-mediated C-Si bond activation, comparable studies have been conducted using germanium, a heavier congener (Scheme 1.1b).

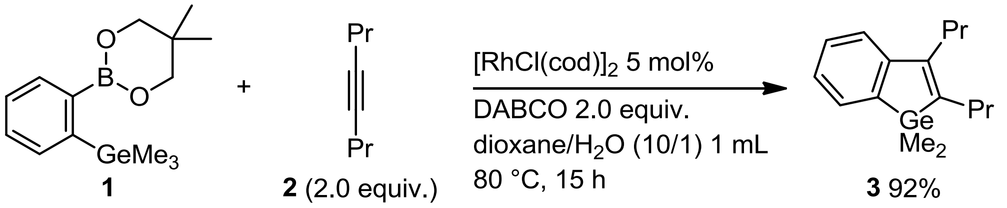
Scheme 1.1. Rh-Catalyzed Synthesis of Benzogermole via C-Ge Bond Cleavage



The Chapter 1 describes the activation of C(sp^3)-Ge bonds in the rhodium-catalyzed annulation of 2-germylphenylboronic esters and alkynes. Although several catalytic reactions involving the activation of C(sp^2)-Ge bonds exist,[2] the corresponding activation of unactivated C(sp^3)-Ge bonds has never been attained with the exception of one specific reaction using trimethylgermyl cyanide.[3]

1.2 Results and Discussion

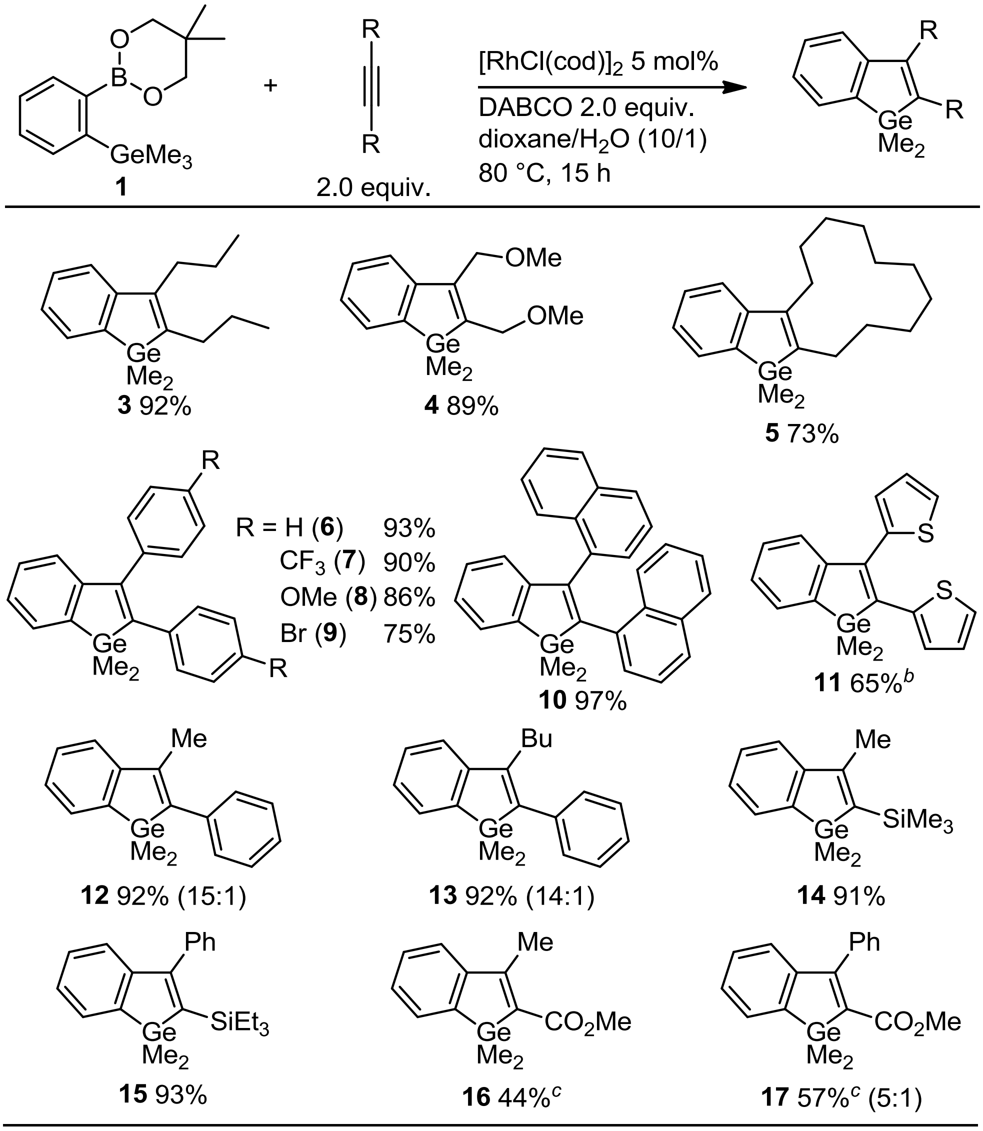
The reaction of 2-trimethylgermylphenylboronic ester **1** with alkyne **2** in the presence of a rhodium catalyst under the conditions typical for the generation of arylrhodium species from arylboron derivatives furnished benzogermole **3** in excellent yield (eq 1.1).



(1.1)

The rhodium-catalyzed C-Ge bond activation reaction proved to be applicable to the synthesis of a diverse array of benzogermoles, all of which were previously unknown compounds and were otherwise difficult to prepare (Table 1.1). In addition to simple aliphatic alkynes, such as **2**, oxygenated cyclicand aliphatic alkynes also participated in this rhodium-catalyzed cyclization to form germoles **4** and **5**, respectively. Aromatic alkynes successfully underwent the reaction irrespective of the electronic and steric nature of the substituents (**6**, **7**, **8**, **9**, and **10**). Notably, bromide remained intact, as in **9**, which allows for further structural modification through, for example, cross-coupling reactions. Germoles bearing heteroaromatics (**11**) can be synthesized by this rhodium catalysis. Several sets of unsymmetrical internal alkynes delivered the corresponding germoles in a regioselective fashion. In the case of alkynes bearing phenyl and alkyl groups, a phenyl group was selectively incorporated at the 2-position of the germole ring (**12** and **13**). Silyl (**14** and **15**) and ester (**16** and **17**) groups are also suitable directors to deliver 2,3-disubstituted germoles bearing these groups at the 2-position irrespective of the C-3 substituents. The regioselectivity observed in the present study is consistent with that obtained in the reported catalytic reactions involving the addition of arylrhodium to alkynes.

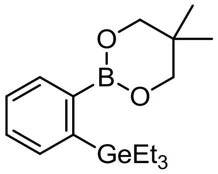
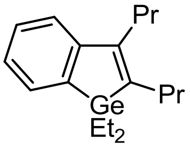
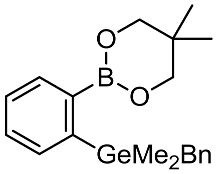
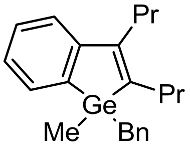
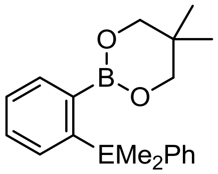
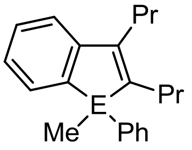
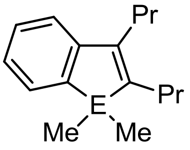
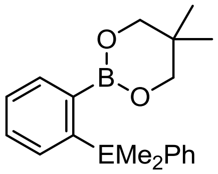
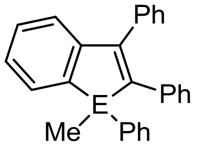
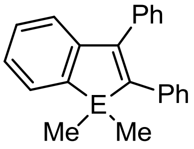
Table 1.1. Scope of Alkynes[a]



[a] Reaction conditions: **1** (0.5 mmol), alkyne (1.0 mmol), $[RhCl(cod)]_2$ (0.05 mmol), and DABCO (1.0 mmol) in dioxane (1 mL) and H_2O (0.1 mL) at 80 °C, 15 h. Isolated yields based on **1** are shown. [b] Run at 100 °C for 72 h using $[RhCl(cod)]_2$ (10 mol%). [c] Run at 100 °C using alkyne (5.0 equiv.), $[RhCl(cod)]_2$ (10 mol%), Na_2CO_3 in place of DABCO.

The scope of the present C-Ge bond activation with respect to the substituent on the germanium was next investigated (Table 1.2). A bulkier triethylgermyl group underwent rhodium-catalyzed annulation to afford the corresponding germole **19**. In the case where the germanium bears both methyl and benzyl groups, as in **20**, a Me-Ge bond was exclusively cleaved to form germole **21**. This observation indicates that the reactivity is largely determined by a steric factor.

Table 1.2. Effect of the Substituents on Germanium[a]

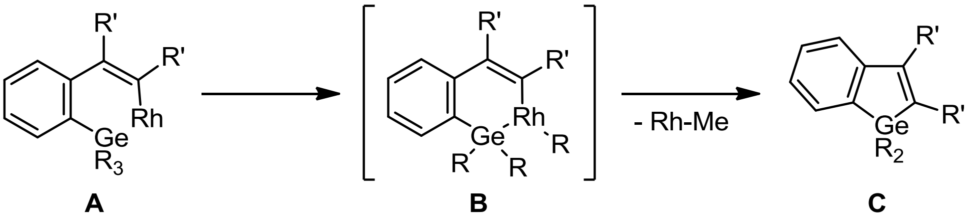
entry	starting material	product
1	 **18**	 **19** 68%
2	 **20**	 **21** 83%
	 **22**	 **23** +  **3 or 24b**
3		E = Ge (**a**) 88% (**23a**:**3** = 1:2.6)
4		E = Si (**b**) 62% (**23b**:**24b** = 1:1.5)[b]
	 **22**	 **25** +  **6 or 26b**
5		E = Ge (**a**) 98% (**25a**:**6** = 1:1.6)[b]
6		E = Si (**b**) 93% (**25b**:**26b** = 1.5:1)[b]

[a] Reaction conditions: boronic ester (0.50 mmol), alkyne (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), and DABCO (1.0 mmol) in dioxane (1 mL) and H_2O (0.1 mL) at 80 °C for 15 h. Isolated yields based on boronic esters are shown. [b] NMR yield based on a boronic ester.

Importantly, Ph-Ge and Me-Ge bonds were activated competitively, as exemplified by the reaction using **22a**. These results are in sharp contrast to the palladium-catalyzed reaction of pentacoordinated $PhMe_2GeF_2^-$ species, wherein a Ph-Ge bond is exclusively activated.[2c] The relative reactivity of Ph-Ge/Me-Ge bonds in this rhodium catalysis was dependent on the structure of the alkyne coupled: the larger alkyne substituent increased the ratio of Me-Ge cleavage (Table 1.2, entry 3 vs 5). Interestingly, the corresponding silicon derivatives exhibited a greater tendency to Me-Si cleavage over Ph-Si (Table 1.2, entry 3 vs 4, entry 5 vs 6).

On the basis of the reactivity profile of a $PhMe_2Ge$ group, C-Ge bond activation is likely to proceed via an oxidative addition pathway[4] (**B** in Scheme 1.2), rather than through a hypervalent germinate intermediate. A larger alkyne substituent R' imposes an increased steric demand around a rhodium center in **A**, which may lead to the greater preference to interact with smaller substituent R. The difference in Me/Ph cleavage ratio between germanium and silicon can be attributed to the difference in the bond length ($Me\text{-}SiMe_3$, 1.875 Å;[5] $Me\text{-}GeMe_3$, 1.945 Å[6]). Due to the slightly shorter C-Si bond length, silicon derivatives are more susceptible to the steric bulk, compared to germanium; therefore a smaller methyl group is activated more favorably.

Scheme 1.2. A Possible Mechanistic Pathway



1.3 Conclusion

In conclusion, the rhodium-catalyzed annulation reaction of 2-germylphenylboronic esters with alkynes is described. The method provides a rapid access to a diverse range of germoles simply by changing the alkyne structure. Importantly, the reaction involves the activation of C(sp^3)-Ge bonds, a process which remained unexplored to date. Fundamental insight into this intriguing bond activation has been gained from the investigation into the activation aptitude of the substituents on germanium and from the comparable reactivity study of the silicon counterparts.

1.4 Experimental Section

General Information.

^{1}H NMR and ^{13}C NMR spectra were recorded using either a JEOL JMN-270 spectrometer, a JEOL ECS-400, Varian Unity-INOVA600 spectrometer in $CDCl_3$. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a Shimadzu GCMS-QP 2010 instrument with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 (Silicycle SiliaFlash F60 (230-400 mesh)). Some compounds were purified by LC-908 HPLC (GPC). Fluorescence spectra were recorded by Shimadzu RF-5300 PC Spectrofluorophotometer.

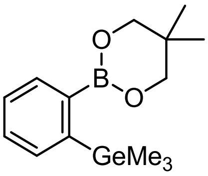
Materials.

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used as received. 1,4-Dioxane was distilled over benzophenone ketyl. 4-Octyne (**2**), 1-phenyl-1-propyne, 1-(trimethylsilyl)-1-propyne and DABCO (1,4-diazabicyclo[2,2,2]octane) were purchased from Wako Pure Chemical Industries, Ltd. Diphenylacetylene, 1-phenyl-1-hexyne, tetrolic acid methyl ester and methyl 3-phenylpropiolate were purchased from Tokyo Chemical Industry Co., Ltd. 1,4-Dimethoxy-2-butyne were purchased from Sigma-Aldrich Co. Sodium carbonate was purchased from Nacalai Tesque.

$[RhCl(cod)]_2$ (CAS: 12092-47-6) was prepared according to literature procedures.[7] Cyclododecyne (CAS: 1129-90-4) was prepared by the method of Brandsma with minor modification.[8] 4,4’-Dimethoxydiphenylacetylene (CAS: 2132-62-9), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (CAS: 119757-51-6), 1,2-bis(4-bromophenyl)ethyne (CAS: 2789-89-1), 1,2-di(naphthalen-1-yl)ethyne (CAS: 20199-29-5) and 1,2-di(thiophen-2-yl)ethyne (CAS: 23975-15-7) were prepared by Sonogashira reaction.[9]

Synthesis of Starting Materials.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylgermane (1)



A dry three-necked flask was charged with a solution of 1,2-dibromobenzene (3.9 g, 16 mmol) in THF/Et_2O (33 mL/33 mL) in a nitrogen atmosphere. The solution was cooled to −110 °C using an EtOH/liquid N_2 bath. A solution of *n*-BuLi in hexane (1.6 M, 12 mL, 20 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min to give a white suspension. A solution of chlorotrimethylgermane (5.0 g, 33 mmol) in

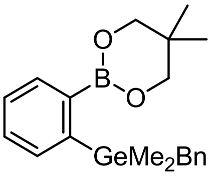
Et_2O (10 mL) was added dropwise to the vigorously stirred suspension. The reaction mixture was stirred at −110 °C to −100 °C for 90 min and allowed to warm slowly to room temperature. The saturated aqueous solution of NH_4Cl was added and the mixture was extracted with Et_2O (20 mL×3). The combined organic layers were washed (brine), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residual yellow oil was distilled using Kugel Rohr apparatus to give (2-bromophenyl)trimethylgermane (4.4 g, 97%, 125 °C-130 °C, 11 mmHg) as a colorless oil.

A dry three-necked flask was charged with a solution of (2-bromophenyl)trimethylgermane (4.4 g, 16 mmol) in toluene/THF (100 mL/25 mL) in a nitrogen atmosphere. The solution was cooled to −78 °C using a MeOH/dry ice bath. A solution of *n*-BuLi in hexane (1.6 M, 13 mL, 21 mmol) was added dropwise to the solution. After the mixture was stirred for an additional 60 min, triisopropyl borate (9.5 mL, 41 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then 1 M HCl solution (50 mL) was added at 0 °C. The mixture was extracted with Et_2O (20 mL×3), and the combined organic layers were washed (brine), dried ($MgSO_4$), filtered, and evaporated in vacuo to produce crude 2-(trimethylgermyl)phenylboronic acid (3.3 g) as a pale yellow solid. A round-bottom flask was chaged with a solution of crude 2-(trimethylgermyl)phenylboronic acid (3.3 g) and 2,2-dimethylpropane-1,3-diol (1.4 g, 14 mmol) in hexane. The reaction mixture was stirred overnight. Then $CaCl_2$ was added and the mixture was stirred for a few hours. The mixture was filtered and evaporated in vacuo. The residual yellow oil was distilled by Kugel Rohl apparatus (100-110 °C, 10 mmHg) then purified by silica gel column chromatography (hexane/EtOAc = 100/1→10/1) to give a titled compound (2.7 g, 8.8 mmol, 55%).

Colorless oil. Rf 0.21 (hexane/EtOAc = 100/1). ^1H NMR ($CDCl_3$, 270.05 MHz) δ: 0.38 (s, 9H), 1.04 (s, 6H), 3.76 (s, 4H), 7.29-7.38 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 6.9

Hz, 1H). ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: 0.5, 22.0, 31.7, 72.0, 127.4, 129.4, 133.5, 134.7, 148.6. IR (neat): 3047 w, 2964 m, 2931 m, 2906 m, 1581 w, 1556 w, 1541 w, 1481 s, 1433 m, 1415 m, 1377 m, 1336 s, 1311 s, 1252 m, 1138 s, 1070 w, 1030 w, 829 m, 764 w, 733 m, 683 w, 650 m, 596 m, 571 w, 503 w, 480 w, 420 w. MS, *m/z* (relative intensity, %): 308 (M^+, 0), 293 (M^+-Me, 44), 292 (24), 291 (35), 290 (11), 289 (25), 225 (26), 224 (13), 223 (21), 221 (15), 207 (30), 206 (15), 205 (24), 203 (15), 117 (12), 91 (12), 69 (100). Exact Mass (CI): Calcd for $C_{14}H_{24}BGeO_2$ 309.1076, found 309.1088.

Benzyl(2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethylgermane (20)



A dry three-necked flask was charged with a solution of 1,2-dibromobenzene (1.5 g, 6.4 mmol) in THF/Et_2O (15 mL/15 mL) in a nitrogen atmosphere. The solution was cooled to −110 °C using an EtOH/liquid N_2 bath. A solution of *n*-BuLi in hexane (1.6 M, 4.4 mL, 7.0 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min to give a white suspension. A solution of benzylchlorodimethylgermane (3.7 g, 12 mmol), prepared from dichlorodimethylgermane and benzylmagnesium bromide,[10] in Et_2O (5 mL) was added dropwise to the vigorously stirred suspension. The reaction mixture was stirred at −110 °C to −100 °C for 90 min and allowed to warm slowly to room temperature. The saturated solution of NH_4Cl in water was added and the mixture was extracted with Et_2O (15 mL×3). The combined organic layers were washed (brine), dried ($MgSO_4$), filtered, and evaporated in vacuo. The residual yellow oil was filtered by silica gel to give crude benzyl(2-bromophenyl)dimethylgermane (3.6 g) as a colorless oil.

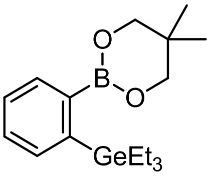
A dry three-necked flask was charged with a solution of crude benzyl(2-bromophenyl)dimethylgermane (3.8 g) in Et_2O (35 mL) in a nitrogen atmosphere.

The solution was cooled to −78 °C using a MeOH/dry ice bath. A solution of *t*-BuLi in hexane (1.6 M, 8.1 mL, 13 mmol) was added dropwise to the solution. After the mixture was stirred for 60 min., a solution of 2-isopropoxy-5,5-dimethyl-1,3,2-dioxaborinane (9.5 mL, 41 mmol) in Et_2O (7 mL) was added dropwise. The reaction mixture was stirred at −78 °C over 60 min. and allowed to warm to 0 °C slowly. After the mixture was stirred for an additional 30 min., chlorotrimethylsilane (1.6 mL, 13 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 20 min. and allowed to warm to room temperature, then stirred overnight. The reaction mixture was filtered by celite and purified by silica gel column chromatography to give a crude product. The crude product was purified by GPC to give a titled compound (2.1 g, 5.5 mmol, 86%).

Colorless oil. Rf 0.14 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.31 (s, 6H), 1.07 (s, 6H), 2.54 (s, 2H), 3.82 (s, 4H), 6.99 (d, J = 6.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 7.34-7.37 (m, 2H), 7.48-7.51 (m, 1H), 7.91-7.93 (m, 1H). ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ: -2.0, 22.0, 26.8, 31.7, 72.1, 123.7, 127.6, 127.98, 128.00, 129.5, 133.9, 135.0, 141.7, 147.1. IR (neat): 3051 w, 3024 w, 2964 m, 2931 m, 1599 w, 1581 w, 1556 w, 1481 m, 1433 m, 1415 m, 1375 m, 1335 s, 1309 s, 1252 s, 1211 w, 1136 s, 1068 w, 1030 w, 999 w, 964 w, 930 w, 904 w, 810 m, 760 m, 735 m, 700 m, 683 w, 650 m, 596 w, 577 w, 503 w, 480 w, 463 w. MS, *m/z* (relative intensity, %): 384 (M^+, 0), 293 (M^+-Bn, 38), 292 (21), 291 (31), 290 (10), 289 (21), 225 (23), 224 (12), 223 (19), 221 (13), 207 (26), 206 (13), 205 (21), 203 (14), 91 (46), 69 (100). Exact Mass (CI): Calcd for $C_{20}H_{28}BGeO_2$ 385.1389, found 385.1389.

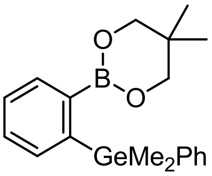
18, **22a** and **22b** were synthesized by the borylation of the corresponding 2-germylbromobenzenes or 2-silylbromobenzene through the procedure described for **20**.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)triethylgermane (18)



Colorless oil. Rf 0.14 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.02 (s, 15H), 1.05 (s, 6H), 3.76 (s, 4H), 7.30-7.35 (m, 2H), 7.48-7.50 (m, 1H), 7.84-7.87 (m, 1H). ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ: 5.7, 9.3, 22.0, 31.7, 72.1, 127.1, 129.1, 134.6, 134.7, 145.4. IR (neat): 2958 m, 2906 m, 2871 m, 1579 w, 1558 w, 1541 w, 1481 m, 1458 m, 1431 m, 1377 m, 1336 m, 1311 s, 1250 m, 1138 s, 1070 w, 1014 w, 970 w, 816 w, 766 w, 739 w, 708 w, 685 w, 652 w, 575 w, 482 w, 420 w. MS, *m/z* (relative intensity, %): 350 (M^+, 0), 323 (11), 322 (10), 321 (M^+-Et, 50), 320 (28), 319 (39), 318 (13), 317 (28), 253 (29), 252 (15), 251 (24), 249 (20), 235 (15), 233 (12), 279 (11), 177 (22), 175 (16), 69 (100). Exact Mass (CI): Calcd for $C_{17}H_{30}BGeO_2$ 351.1545, found 351.1555.

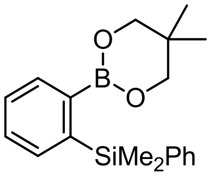
(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethyl(phenyl)germane (22a)



White solid. Mp = 89-90 °C. Rf 0.24 (hexane/EtOAc = 50/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.66 (s, 6H), 0.87 (s, 6H), 3.49 (s, 4H), 7.30-7.34 (m, 3H), 7.35-7.38 (m, 2H), 7.46-7.48 (m, 2H), 7.50-7.52 (m, 1H), 7.86-7.88 (m, 1H). ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ: -0.8, 21.8, 31.4, 71.6, 127.71, 127.727, 127.734, 129.4, 133.4, 134.5, 134.7, 143.2, 145.9. IR (KBr): 3064 m, 3047 m, 3005 m, 2966 s, 2951 s, 2908 s, 2871 m, 1579 m, 1481 s, 1431 s, 1375 s, 1336 s, 1313 s, 1250 s, 1165 m, 1134 s, 1092 m, 1065 m, 1028 m, 995 w, 960 w, 810 s, 769 m, 731 s, 700 s, 667 m, 646 s, 604 m, 577 m, 501 w, 472 m. MS, *m/z* (relative intensity, %): 370 (M^+, 0), 357 (11), 356 (12), 355 (M^+-Me, 51), 354 (29), 353 (40), 352 (13), 351 (28), 293 (23), 292 (12), 291 (18), 289 (14), 287 (11), 269 (24), 268 (12), 267 (19), 265 (12), 209 (32), 208

(15), 207 (31), 205 (22), 165 (14), 163 (12), 151 (11), 149 (13), 91 (26), 69 (100). Exact Mass (CI): Calcd for $C_{19}H_{26}BGeO_2$ 371.1232, found 371.1234.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethyl(phenyl)silane (22b)

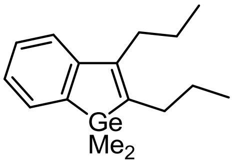


White solid. Mp = 73-75 °C. Rf 0.24 (hexane/EtOAc = 50/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.55 (s, 6H), 0.81 (s, 6H), 3.38 (s, 4H), 7.31-7.32 (m, 3H), 7.37-7.40 (m, 2H), 7.46-7.48 (m, 2H), 7.62-7.64 (m, 1H), 7.78-7.80 (m, 1H). ^{13}C NMR ($CDCl_3$, 150.83 MHz) δ: -0.4, 21.8, 31.3, 71.5, 127.5, 128.1, 128.2, 129.0, 133.7, 133.9, 135.5, 141.0, 143.0. IR (KBr): 3068 m, 3047 m, 2951 s, 2902 m, 1581 w, 1481 s, 1431 s, 1377 m, 1336 s, 1313 s, 1244 s, 1163 m, 1134 s, 1111 s, 1070 m, 1026 m, 995 w, 958 w, 822 s, 769 s, 735 s, 698 s, 644 s, 501 w, 480 m, 447 m, 420 w. MS, *m/z* (relative intensity, %): 324 (M^+, 0), 310 (25), 309 (M^+-Me, 100), 308 (24), 267 (30), 253 (13), 247 (37), 223 (43), 211 (16), 209 (19), 189 (15), 163 (52), 162 (14), 161 (11), 120 (10), 119 (87), 105 (18), 93 (24), 69 (95), 53 (10). Exact Mass (CI): Calcd for $C_{19}H_{26}BO_2Si$ 325.1790 found 325.1804.

General Procedure for the Rh-Catalyzed Synthesis of 3 (Table 1.1).

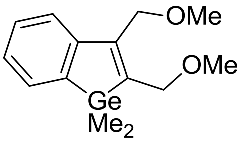
An oven-dried 5 mL screw-capped vial was charged with (2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylgermane (**1**, 0.15 g, 0.50 mmol), 4-octyne (**2**, 0.11 g, 1.0 mmol), DABCO (0.11 g, 1.0 mmol), $[RhCl(cod)]_2$ (12 mg, 0.025 mmol), 1,4-dioxane (1 mL) and H_2O (0.1 mL) under a gentle stream of nitrogen. The vessel was heated in an oil bath at 80 °C for 15 h followed by cooling. The contents were subjected to flash chromatography (hexane) to give 1,1-dimethyl-2,3-dipropyl-1*H*-benzo[*b*]germole (**3**, 0.14 g, 94%) as a white solid.

1,1-Dimethyl-2,3-dipropyl-1*H*-benzo[*b*]germole (3).



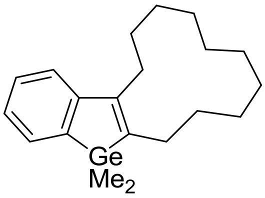
Colorless oil. Rf 0.63 (hexane). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ: 0.47 (s, 6H), 0.88-1.01 (m, 6H), 1.46-1.60 (m, 4H), 2.43-2.55 (m, 4H), 7.14-7.20 (m, 1H), 7.30-7.32 (m, 2H), 7.49 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ: -2.7, 14.39, 14.42, 22.1, 24.0, 29.1, 33.1, 121.7, 125.6, 128.8, 131.4, 140.6, 144.7, 147.1, 149.0. IR (neat): 3053 m, 2958 s, 2927 s, 2870 s, 1583 m, 1556 w, 1462 s, 1441 s, 1377 m, 1336 w, 1298 w, 1271 m, 1234 m, 1186 w, 1161 w, 1122 w, 1093 w, 1032 w, 835 s, 796 s, 762 s, 725 s, 648 w, 602 s, 582 m, 428 w. MS *m/z* (relative intensity, %): 292 (M^++2, 12), 290 (M^+, 69), 289 (M^+-1, 20), 288 (M^+-2, 49), 286 (M^+-4, 36), 277 (14), 276 (10), 275 (81), 274 (23), 273 (58), 271 (43), 261 (11), 259 (11), 247 (27), 246 (10), 245 (21), 243 (16), 233 (18), 231 (18), 229 (14), 219 (12), 217 (19), 215 (16), 186 (14), 185 (43), 184 (17), 157 (55), 155 (35), 143 (71), 142 (23), 141 (38), 129 (72), 128 (58), 127 (13), 115 (67), 107 (17), 105 (100), 104 (21), 103 (79), 101 (62), 91 (39), 89 (77), 88 (13), 87 (55), 85 (37). Exact Mass (EI): Calcd for $C_{16}H_{24}Ge$ 290.1090, found 290.1092.

2,3-Bis(methoxymethyl)-1,1-dimethyl-1*H*-benzo[*b*]germole (4)



Colorless oil. Rf 0.43 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.54 (s, 6H), 3.38 (s, 6H), 4.38 (s, 2H), 4.51 (s, 2H), 7.19-7.23 (m, 1H), 7.30-7.35 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.8, 57.9, 58.4, 67.1, 72.4, 122.6, 126.4, 128.9, 131.6, 141.1, 142.1, 147.5, 148.9. IR (neat): 3051 m, 2981 s, 2914 s, 2885 s, 2816 s, 1583 m, 1560 w, 1444 s, 1362 s, 1302 m, 1273 m, 1232 m, 1192 s, 1161 s, 1103 s, 955 s, 908 m, 837 s, 802 s, 764 s, 725 s, 607 s, 584 s, 526 w, 484 w, 424 w. MS, *m/z* (relative intensity, %): 264 (M^++1-OMe, 15), 262 (27), 260 (20), 258 (10), 251 (16), 250 (11), 249 (83), 248 (30), 247 (100), 246 (21), 245 (75), 243 (26), 232 (10), 219 (16), 217 (38), 216 (13), 215 (44), 213 (29), 211 (11), 189 (14), 187 (12), 159 (12), 141 (12), 135 (17), 133 (13), 131 (13), 129 (34), 128 (81), 127 (13), 123 (10), 121 (31), 119 (25), 117 (23), 116 (13), 115 (52), 107 (13), 105 (55), 104 (15), 103 (45), 101 (36), 91 (17), 89 (36), 87 (25), 85 (17), 75 (11). Exact Mass (EI): Calcd for $C_{14}H_{20}GeO_2$ 294.0675, found 294.0677.

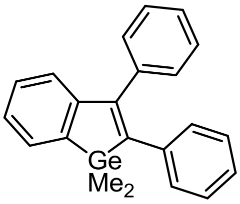
5,5-Dimethyl-6,7,8,9,10,11,12,13,14,15-decahydro-5*H*-benzo[*b*]cyclododeca[*d*]germole (5)



White solid. Mp = 68-70 °C. Rf 0.43 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.48 (s, 6H), 1.29-1.74 (m, 16H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.64 (t, *J* = 6.6 Hz, 2H), 7.17-7.20 (m, 1H), 7.31-7.38 (m, 2H), 7.52 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.8, 21.9, 23.1, 23.5, 23.9, 25.0, 25.6, 25.8, 26.8, 27.7, 27.8, 122.3, 125.5, 128.8, 131.3, 140.6, 145.4, 146.4, 149.1. IR (KBr): 3064 w, 3051 w, 2968 m, 2916 s, 2848 s, 1581 w, 1466 m, 1441 m, 1292 w, 1273 w, 1115 w, 831 m, 795 m, 760 m, 725 m, 652 w, 600 m, 580 m, 482 w. MS, *m/z* (relative intensity, %): 346 (M^++2, 16), 345 (M^++1, 17), 344 (M^+, 81), 343 (M^+-1, 29), 342 (M^+-2, 59), 340 (M^+-4, 44), 331 (18), 330 (18), 329 (87), 328 (31), 327 (67), 325 (50), 245 (23), 243 (21), 241 (17), 240 (19), 239 (42), 238 (12), 237 (20), 233 (22), 231 (26), 229 (22), 227 (11), 221 (14), 220 (67), 219 (44), 218 (55), 217 (41), 216 (43), 215 (32), 213 (19), 211 (12), 207 (21), 205 (58), 204 (17), 203 (49), 201 (39), 197 (11), 195 (11), 193 (15), 191 (24), 189 (24), 187 (15), 183 (16), 181 (21), 169 (23), 167 (20), 165 (12), 157 (15), 155 (47), 153 (14), 143 (38), 142 (29), 141 (83), 131 (16), 130 (17), 129 (67), 128 (50), 127 (13), 117

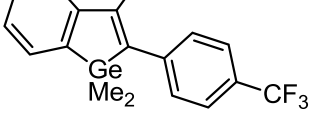
(31), 115 (61), 107 (22), 105 (89), 104 (25), 103 (67), 101 (53), 95 (17), 91 (61), 89 (100), 88 (20), 87 (74), 85 (53), 81 (28), 79 (11), 69 (13), 67 (36), 55 (54). Exact Mass (EI): Calcd for $C_{20}H_{30}Ge$ 344.1559, found 344.1555.

1,1-Dimethyl-2,3-diphenyl-1*H*-benzo[*b*]germole (6)



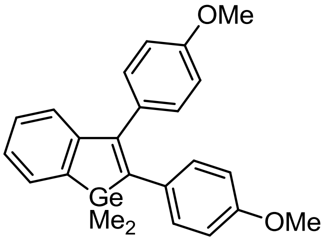
White solid. Mp = 103-104 °C. Rf 0.21 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.66 (s, 6H), 6.95-6.97 (m, 2H), 7.02-7.07 (m, 2H), 7.10-7.14 (m, 2H), 7.19-7.21 (m, 2H), 7.25-7.27 (m, 2H), 7.30-7.37 (m, 3H), 7.61-7.63 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.5, 124.8, 125.7, 126.7, 126.9, 127.9, 128.4, 128.7, 129.0, 129.8, 131.6, 138.7, 140.37, 140.41, 144.9, 149.76, 149.82. IR (KBr): 3072 m, 3051 m, 3018 w, 2991 w, 2968 w, 2906 w, 1595 w, 1547 w, 1489 m, 1441 m, 1415 w, 1296 w, 1236 w, 1153 w, 1120 w, 1074 w, 1030 w, 978 w, 908 w, 835 m, 800 m, 766 s, 746 m, 725 m, 700 s, 665 w, 596 m, 482 w, 413 w. MS, *m/z* (relative intensity, %): 360 (M^++2, 13), 359 (M^++1, 14), 358 (M^+, 61), 357 (22), 356 (M^+-2, 44), 354 (32), 345 (22), 344 (M^+-4, 22), 343 (100), 342 (38), 341 (76), 340 (14), 339 (60), 254 (22), 253 (43), 252 (73), 250 (13), 151 (11). Exact Mass (EI): Calcd for $C_{22}H_{20}Ge$ 358.0777, found 358.0774.

1,1-Dimethyl-2,3-bis(4-(trifluoromethyl)phenyl)-1*H*-benzo[*b*]germole (7)



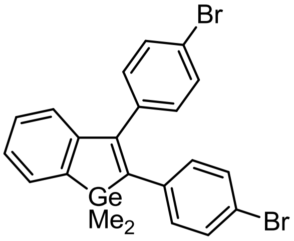
White solid. Mp = 130-131 °C. Rf 0.40 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.67 (s, 6H), 6.97-6.99 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.29-7.32 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.64-7.66 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.7, 124.9, 124.1 (q, *J* = 272.1 Hz), 124.2 (q, *J* = 272.1 Hz), 125.1 (q, *J* = 2.8 Hz), 125.5 (q, *J* = 2.8 Hz), 127.5, 127.7 (q, *J* = 31.6 Hz), 128.4, 129.3, 129.4 (q, *J* = 32.6 Hz), 130.1, 132.0, 140.2, 141.8, 144.0, 145.2, 148.4, 150.0. IR (KBr): 3059 w, 2995 w, 2924 w, 1610 m, 1574 w, 1550 w, 1441 w, 1408 w, 1323 s, 1242 w, 1167 s, 1113 s, 1066 s, 1016 w, 980 w, 849 m, 800 w, 756 w, 727 w, 692 w, 669 w, 609 w, 418 w. MS, *m/z* (relative intensity, %): 494 (M^+, 47), 493 (15), 492 (M^+-2, 33), 490 (M^+-4, 22), 481 (18), 480 (20), 479 (100), 478 (36), 477 (76), 476 (12), 475 (59), 372 (10), 371 (53), 351 (12), 320 (12), 301 (21), 252 (10). Exact Mass (EI): Calcd for $C_{24}H_{18}F_6Ge$ 494.0524, found 454.0529.

2,3-Bis(4-methoxyphenyl)-1,1-dimethyl-1*H*-benzo[*b*]germole (8)



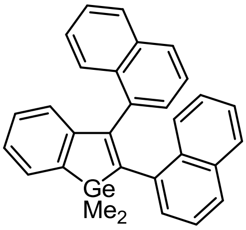
White solid. Mp = 114-115 °C. Rf 0.37 (hexane/CH_2Cl_2 = 2/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.65 (s, 6H), 3.75 (s 3H), 3.85 (s, 3H), 6.68-6.71 (m, 2H), 6.91-6.94 (m, 4H), 7.02-7.04 (m, 1H), 7.12-7.15 (m, 2H), 7.23-7.26 (m, 2H), 7.59-7.61 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.3, 55.1, 55.2, 113.4, 114.0, 124.5, 126.4, 129.0, 130.1, 130.9, 131.2, 131.5, 132.8, 140.0, 143.8, 148.0, 150.3, 157.5, 158.4. IR (KBr): 3057 m, 3030 m, 3002 m, 2929 m, 2904 m, 2835 m, 1604 s, 1576 m, 1545 m, 1504 s, 1458 s, 1441 s, 1414 m, 1282 s, 1248 s, 1176 s, 1151 m, 1107 m, 1032 s, 978 m, 835 s, 802 s, 783 m, 754 m, 727 m, 604 m, 577 m, 501 w, 418 w. MS, *m/z* (relative intensity, %): 420 (M^++2, 21), 419 (M^++1, 23), 418 (M^+, 100), 417 (37), 416 (M^+-2, 72), 415 (11), 414 (M^+-4, 51), 405 (19), 404 (20), 403 (88), 402 (32), 401 (63), 399 (47), 328 (11), 327 (22), 314 (12), 299 (20), 283 (17), 252 (21), 240 (21), 239 (52), 227 (12), 226 (16), 181 (17), 179 (13), 157 (16), 121 (26), 105 (26), 103 (19), 101 (17), 89 (12). Exact Mass (EI): Calcd for $C_{24}H_{24}GeO_2$ 418.0988, found 418.0991.

2,3-Bis(4-bromophenyl)-1,1-dimethyl-1*H*-benzo[*b*]germole (9)



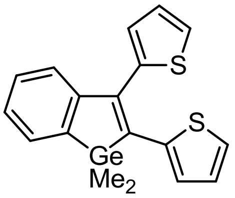
White solid. Mp = 173-174 °C. Rf 0.31 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.64 (s, 6H), 6.80 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.26-7.28 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.7, 119.7, 121.2, 124.7, 127.1, 129.2, 130.0, 131.2, 131.5, 131.7, 131.8, 137.0, 139.2, 140.2, 144.5, 148.8, 149.1. IR (KBr): 3055 m, 2908 w, 1587 m, 1545 m, 1481 s, 1441 m, 1389 m, 1300 m, 1230 w, 1149 w, 1103 m, 1070 s, 1011 s, 839 s, 820 s, 777 s, 725 s, 694 m, 673 w, 602 m, 582 m, 538 w, 503 m, 488 m, 424 m. MS, *m/z* (relative intensity, %): 519 (11), 518 (45), 517 (28), 516 (M^++2, 94), 515 (M^++1, 35), 514 (M^+, 93), 513 (21), 512 (M^+-2, 57), 510 (M^+-4, 17), 504 (11), 503 (48), 502 (28), 501 (98), 500 (36), 499 (100), 498 (20), 497 (61), 495 (18), 412 (15), 368 (12), 366 (10), 265 (12), 253 (20), 252 (86), 251 (17), 250 (45). Exact Mass (EI): Calcd for $C_{22}H_{18}Br_2Ge$ 513.8987, found 513.8984.

1,1-Dimethyl-2,3-di(naphthalen-1-yl)-1*H*-benzo[*b*]germole (10)



White solid. Mp = 169-170 °C. Rf 0.21 (hexane/CH_2Cl_2 = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.61 (s, 3H), 0.67 (s, 3H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 7.07-7.18 (m, 4H), 7.28-7.42 (m, 5H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.58-7.62 (m, 1H), 7.68-7.75 (m, 3H), 7.88 (d, *J* = 7.6 Hz, 1H), 8.02-8.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.8, -2.1, 123.4, 125.0, 125.3, 125.4, 125.5, 125.6, 126.4, 126.5, 126.8, 127.2, 128.0, 128.1, 129.2, 131.4, 131.7, 131.9, 133.2, 133.3, 136.0, 139.2, 140.7, 147.6, 149.4, 150.6. IR (KBr): 3049 m, 2991 m, 2904 m, 1581 m, 1502 m, 1437 m, 1389 s, 1331 w, 1292 m, 1248 m, 1155 w, 1119 w, 1093 w, 1053 w, 1012 m, 949 m, 904 w, 839 m, 798 s, 775 s, 723 s, 669 m, 634 w, 609 m, 580 m, 522 m, 503 m, 424 m. MS, *m/z* (relative intensity, %): 460 (M^++2, 24), 459 (M^++1, 31), 458 (M^+, 100), 457 (42), 456 (M^+-2, 71), 455 (17), 454 (M^+-4, 51), 444 (13), 443 (42), 442 (18), 441 (33), 439 (23), 354 (15), 353 (37), 352 (45), 351 (25), 350 (32), 315 (42), 314 (15), 313 (31), 311 (23), 277 (19), 276 (24), 226 (10). Exact Mass (EI): Calcd for $C_{30}H_{24}Ge$ 458.1090, found 458.1088.

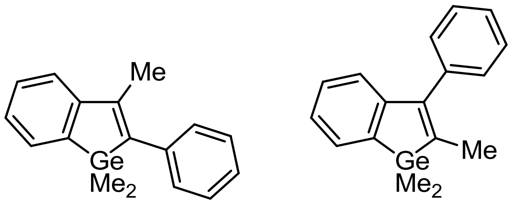
1,1-Dimethyl-2,3-di(thiophen-2-yl)-1*H*-benzo[*b*]germole (11)



White solid. Mp = 124-125 °C. Rf 0.26 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.76 (s, 6H), 6.95-7.01 (m, 4H), 7.19-7.21 (m, 1H), 7.24-7.32 (m, 3H), 7.58-7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -1.8, 124.4, 126.1, 126.7, 127.2, 127.5, 127.99, 128.05, 128.8, 129.5, 131.4, 138.1, 138.3, 139.2, 141.3, 142.9, 150.5. IR (KBr): 3059 w, 2904 w, 1576 w, 1437 m, 1415 w, 1275 m, 1236 w, 1209 w, 1115 w, 1057 w, 1034 w, 850 m, 827 m, 800 m, 773 m, 704 s, 606 m, 582 m, 476 w, 424 w. MS, *m/z* (relative intensity, %): 372 (M^++2, 29), 371 (M^++1, 22), 370 (M^+, 100), 369 (35), 368 (M^+-2, 73), 367 (11), 366 (M^+-4, 51), 355 (39), 354

(12), 353 (30), 351 (20), 321 (22), 319 (15), 316 (10), 266 (48), 265 (12), 249 (25), 235 (19), 234 (99), 233 (17), 232 (18), 221 (17), 215 (10), 208 (25), 189 (19), 117 (17), 104 (21), 89 (17), 87 (13). Exact Mass (EI): Calcd for $C_{18}H_{16}GeS_2$ 369.9905, found 369.9913.

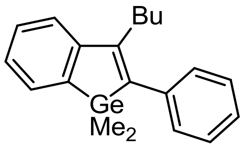
1,1,3-Trimethyl-2-phenyl-1*H*-benzo[*b*]germole (12)

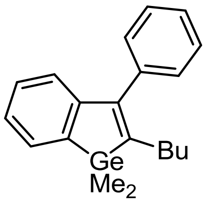


This compound was obtained as a regioisomeric mixture of **12** and **12’** (15:1) determined by NMR. White solid. Mp = 61-63 °C. Rf 0.43 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.54 (s, 6H), 2.16 (s, 3H), 7.16-7.29 (m, 4H), 7.35-7.46 (m, 4H), 7.57 (d, *J* = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.1, 14.6, 122.6, 125.5, 126.6, 127.9, 128.2, 129.1, 131.4, 140.4, 141.8, 143.9, 144.2, 149.6. IR (KBr): 3074 w, 3049 s, 3018 m, 2985 m, 2933 m, 2906 m, 1593 m, 1487 m, 1439 s, 1365 m, 1279 m, 1232 m, 1157 w, 1122 m, 1070 m, 1028 m, 926 w, 894 w, 839 m, 793 s, 760 s, 723 s, 702 s, 602 s, 582 s, 540 w, 499 m, 472 m, 440 w. MS, *m/z* (relative intensity, %): 296 (M^+, 49), 295 (16), 294 (M^+-2, 36), 292 (M^+-4, 26), 283 (21), 282 (16), 281 (100), 280 (34), 279 (78), 278 (10), 277 (60), 265 (19), 263 (16), 261 (12), 191 (29), 189 (16), 165 (10), 115 (12), 89 (15). Exact Mass (EI): Calcd for $C_{17}H_{18}Ge$ 296.0620, found 296.0617. The regiochemistry of **12** was determined based on NOE experiments.

The formation of **12’** was confirmed by GCMS *m/z* (relative intensity, %): 296 (M^+, 41), 295 (11), 294 (M^+-2, 29), 292 (M^+-4, 20), 283 (18), 282 (12), 281 (100), 280 (30), 279 (75), 277 (56), 265 (11), 191 (30), 189 (16), 165 (11), 115 (12), 89 (20), 87 (12).

3-Butyl-1,1-dimethyl-2-phenyl-1*H*-benzo[*b*]germole (13)

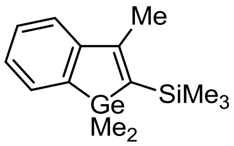




This compound was obtained as a regioisomeric mixture of **13** and **13’** (14:1) determined by NMR. Colorless oil. Rf 0.43 (hexane).^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.51 (s, 6H), 0.84-0.88 (m, 3H), 1.30-1.36 (m, 2H), 1.52-1.60 (m, 2H), 2.53 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.18-7.28 (m, 2H), 7.33-7.41 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.3, 13.9, 23.0, 27.8, 31.7, 122.9, 125.4, 126.3, 127.4, 128.2, 129.0, 131.7, 141.1, 142.1, 144.1, 148.5, 149.0. IR (neat): 3055 m, 3020 m, 2956 s, 2927 s, 2864 s, 1599 m, 1579 m, 1554 w, 1489 m, 1462 m, 1441 m, 1415 w, 1379 w, 1273 w, 1234 w, 1124 w, 1070 w, 1032 w, 920 w, 837 m, 796 m, 762 s, 727 s, 700 s, 606 m, 584 m, 542 w, 484 w, 426 w. MS, *m/z* (relative intensity, %): 340 (M^++2, 10), 339 (M^++1, 10), 338 (M^+, 49), 337 (17), 336 (M^+-2, 35), 334 (M^+-4, 26), 325 (21), 324 (19), 323 (100), 322 (35), 321 (74), 320 (10), 319 (54), 296 (40), 295 (15), 294 (29), 292 (22), 281 (30), 280 (11), 279 (29), 277 (23), 265 (29), 264 (10), 263 (28), 261 (19), 205 (11), 203 (14), 202 (13), 192 (14), 191 (59), 189 (20), 165 (13), 115 (11), 91 (25), 90 (26), 87 (18), 85 (12). Exact Mass (EI): Calcd for $C_{20}H_{24}Ge$ 338.1090, found 338.1082. The regiochemistry of **13** was determined based on NOE experiments.

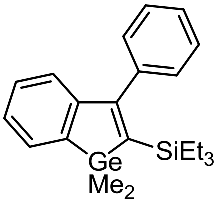
The formation of **13’** was confirmed by GCMS *m/z* (relative intensity, %): 338 (M^+, 50), 205 (23), 191 (100).

Trimethyl(1,1,3-trimethyl-1*H*-benzo[*b*]germol-2-yl)silane (14)



Colorless oil. Rf 0.80 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.24 (s, 9H), 0.49 (s, 6H), 2.33 (s, 3H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -2.3, 0.9, 19.6, 122.1, 126.7, 128.8, 131.0, 140.5, 143.2, 149.6, 158.4. IR (neat): 3060 w, 2954 m, 2908 w, 1537 m, 1437 m, 1369 w, 1250 s, 1128 w, 1093 w, 1030 w, 1005 w, 895 s, 839 s, 795 w, 764 m, 723 w, 688 w, 636 w, 602 w, 584 w, 488 w, 420 w. MS, *m/z* (relative intensity, %): 292 (M^+, 28), 290 (M^+-2, 20), 288 (M^+-4, 14), 279 (23), 278 (18), 277 (93), 276 (31), 275 (70), 273 (52), 189 (12), 188 (35), 187 (10), 174 (14), 173 (84), 145 (46), 131 (19), 115 (19), 97 (10), 89 (14), 73 (100), 59 (27). Exact Mass (EI): Calcd for $C_{14}H_{22}GeSi$ 292.0703, found 292.0710. The regiochemistry of **14** was determined based on NOE experiments.

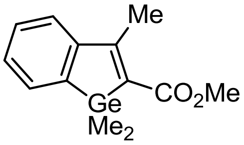
(1,1-Dimethyl-3-phenyl-1*H*-benzo[*b*]germol-2-yl)triethylsilane (15)



Colorless oil. Rf 0.49 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.41 (q, *J* = 7.8 Hz, 6H), 0.65 (s, 6H), 0.88 (t, *J* = 7.8 Hz, 9H), 6.85-6.86 (m, 1H), 7.22-7.30 (m, 4H), 7.40-7.45 (m, 3H), 7.64-7.66 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -1.8, 4.4, 7.6, 124.7, 126.8, 127.0, 127.8, 128.66, 128.74, 131.1, 141.5, 142.0, 143.0, 150.0, 164.8. IR (neat): 3055 s, 2953 s, 2908 s, 2873 s, 2808 m, 1574 m, 1523 s, 1485 s, 1460 s, 1439 s, 1417 s, 1377 m, 1273 s, 1234 s, 1159 m, 1120 m, 1070 m, 1007 s, 974 s, 910 s, 839 s, 787 s, 741 s, 723 s, 700 s, 677 s, 598 s, 582 s, 496 m, 482 m, 413 s. MS, *m/z* (relative intensity, %): 396 (M^+, 0), 369 (M^++2-Et, 23), 368 (M^++1-Et, 25), 367 (M^+-Et, 100), 366 (37), 365 (73), 364 (12), 363 (53), 339 (28), 337 (20), 335 (15), 311 (26), 309 (21), 307 (16), 221 (25), 207 (11), 151 (12), 149 (11), 148 (12), 147 (34), 146 (18), 145 (16), 135 (16), 105 (13), 87 (12), 73 (16), 59 (34). Exact Mass (EI):

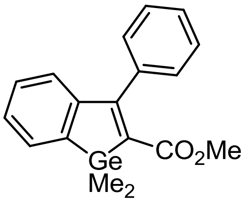
Calcd for $C_{22}H_{30}GeSi$ 396.1329, found 396.1328. The regiochemistry of **15** was determined based on NOE experiments.

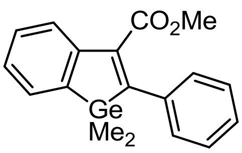
Methyl 1,1,3-trimethyl-1*H*-benzo[*b*]germole-2-carboxylate (16)



Colorless oil. Rf 0.20 (hexane/EtOAc = 50/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.55 (s, 6H), 2.61 (s, 3H), 3.79 (s, 3H), 7.37-7.42 (m, 2H), 7.55-7.61 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.2, 15.4, 51.5, 124.3, 129.0, 129.1, 131.7, 131.8, 141.5, 148.1, 161.8, 169.5. IR (neat): 3053 w, 2987 w, 2947 w, 2912 w, 1703 s, 1585 m, 1554 m, 1437 m, 1369 w, 1302 m, 1273 m, 1211 s, 1105 m, 1055 m, 957 w, 841 w, 800 w, 773 m, 723 w, 611 w, 588 w. MS, *m/z* (relative intensity, %): 278 (M^+, 30), 276 (M^+-2, 22), 274 (M^+-4, 15), 265 (15), 263 (73), 262 (22), 261 (53), 259 (40), 247 (16), 245 (11), 235 (22), 234 (12), 233 (100), 232 (31), 231 (80), 229 (60), 220 (15), 219 (12), 218 (19), 217 (16), 216 (16), 215 (13), 203 (13), 201 (10), 189 (18), 187 (16), 185 (11), 129 (12), 128 (23), 116 (27), 115 (95), 114 (13), 105 (20), 103 (18), 101 (16), 91 (14), 89 (42), 87 (28), 85 (18). Exact Mass (EI): Calcd for $C_{13}H_{16}GeO_2$ 278.0362, found 278.0363. The regiochemistry of **16** was determined based on NOE experiments.

Methyl 1,1-dimethyl-3-phenyl-1*H*-benzo[*b*]germole-2-carboxylate (17)

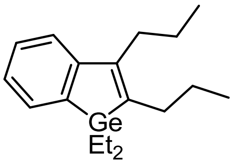




This compound was obtained as a regioisomeric mixture of **17**and **17’** (5:1) determined by NMR. White solid. Mp = 51-54 °C. Rf 0.26 (hexane/EtOAc = 50/1). The followings are the data for **17**. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.69 (s, 6H), 3.64 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.26-7.31 (m, 2H), 7.35-7.49 (m, 5H), 7.63 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.0, 51.4, 126.9, 127.5, 127.9, 128.0, 128.96, 129.04, 131.9, 134.0, 137.9, 141.4, 148.0, 163.3, 168.5. IR (KBr): 3053 w, 2985 w, 2945 w, 2910 w, 1714 s, 1601 w, 1577 m, 1552 m, 1491 w, 1439 m, 1286 m, 1207 s, 1155 m, 1120 w, 1070 m, 1024 w, 843 w, 806 m, 775 m, 727 m, 702 m, 611 m, 586 w, 424 w. MS, *m/z* (relative intensity, %): 342 (M^++2, 11), 341 (M^++1, 10), 340 (M^+, 64), 339 (M^+-1, 24), 338 (M^+-2, 46), 336 (M^+-4, 34), 327 (20), 326 (16), 325 (94), 324 (32), 323 (70), 321 (52), 309 (33), 308 (14), 307 (24), 305 (17), 297 (23), 296 (17), 295 (100), 294 (36), 293 (77), 292 (12), 291 (57), 283 (12), 282 (32), 281 (32), 280 (38), 279 (33), 278 (30), 277 (20), 267 (33), 265 (38), 263 (30), 252 (12), 251 (34), 250 (22), 249 (30), 248 (11), 247 (20), 205 (16), 191 (22), 189 (19), 178 (26), 177 (10), 176 (19), 175 (17), 165 (18), 151 (13), 147 (14), 105 (33), 103 (23), 101 (22), 91 (18), 89 (54), 87 (41), 85 (28). Exact Mass (EI): Calcd for $C_{18}H_{18}GeO_2$ 340.0519, found 340.0521. The regiochemistry of **17** was determined based on NOE experiments.

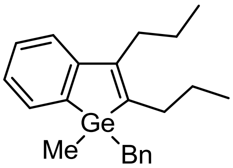
The formation of **17'** was confirmed by GCMS, *m/z* (relative intensity, %): 340 (M^+, 100), 338 (55), 336 (33), 325 (76), 323 (51), 321 (10), 267 (22), 265 (35), 263 (56).

1,1-Diethyl-2,3-dipropyl-1*H*-benzo[*b*]germole (19)



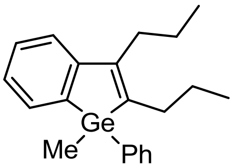
Colorless oil Rf 0.51 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.95-1.00 (m, 6H), 1.02-1.16 (m, 10H), 1.46-1.58 (m, 4H), 2.43 (t, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 7.13-7.18 (m, 1H), 7.30 (t, *J* = 3.6 Hz, 2H), 7.47 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 6.2, 9.3, 14.3, 14.5, 22.2, 24.1, 29.1, 33.7, 121.7, 125.3, 128.6, 132.2, 138.8, 143.3, 148.2, 149.8. IR (neat): 3055 m, 2956 s, 2927 s, 2870 s, 1581 w, 1556 w, 1458 s, 1377 m, 1338 w, 1271 w, 1219 w, 1093 w, 1018 m, 964 w, 766 m, 733 m, 698 m, 577 m, 484 w, 428 w. MS, *m/z* (relative intensity, %): 318 (M^+, 26), 316 (M^+-2, 19), 314 (M^+-4, 13), 291 (20), 290 (17), 289 (100), 288 (33), 287 (75), 285 (57), 261 (28), 259 (23), 257 (16), 185 (10), 143 (16), 141 (13), 129 (22), 128 (18), 115 (23), 103 (11), 91 (11), 89 (13). Exact Mass (EI): Calcd for $C_{18}H_{28}Ge$ 318.1403, found 318.1402.

1-Benzyl-1-methyl-2,3-dipropyl-1*H*-benzo[*b*]germole (21)



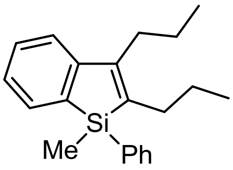
Colorless oil. Rf 0.34 (hexane). ^1H NMR ($CDCl_3$, 399.78 MHz) δ: 0.43 (s, 3H), 0.91-0.98 (m, 6H), 1.41-1.56 (m, 4H), 2.27-2.35 (m, 1H), 2.42-2.57 (m, 5H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.07-7.14 (m, 2H), 7.20-7.23 (m, 3H), 7.28-7.33 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -4.7, 14.37, 14.43, 22.1, 24.2, 24.5, 29.1, 33.3, 121.8, 124.3, 125.6, 127.9, 128.2, 129.0, 132.1, 139.0, 140.0, 143.4, 147.7, 148.8. IR (neat): 3059 m, 3024 m, 2958 s, 2927 s, 2870 m, 1599 m, 1581 w, 1556 w, 1493 m, 1456 m, 1415 w, 1377 w, 1338 w, 1273 w, 1234 w, 1207 w, 1057 w, 1030 w, 812 m, 762 s, 725 m, 698 m, 590 w, 465 m, 424 w. MS, *m/z* (relative intensity, %): 366 (M^+, 8), 277 (22), 276 (16), 275 (100), 274 (33), 273 (76), 272 (10), 271 (60), 143 (12), 129 (15), 128 (11), 115 (13), 91 (33), 89 (24), 87 (18), 85 (12). Exact Mass (EI): Calcd for $C_{22}H_{28}Ge$ 366.1403, found 366.1402.

1-Methyl-1-phenyl-2,3-dipropyl-1*H*-benzo[*b*]germole (23a)



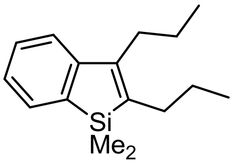
Colorless oil. Rf 0.34 (hexane). ^1H NMR ($CDCl_3$, 399.78 MHz) δ: 0.81 (d, *J* = 0.8 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 1.40-1.53 (m, 2H), 1.54-1.65 (m, 2H), 2.38-2.45 (m, 1H), 2.50-2.57 (m, 1H), 2.61 (t, *J* = 7.8 Hz, 2H), 7.17-7.20 (m, 1H), 7.32-7.39 (m, 5H), 7.44-7.50 (m, 3H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: -5.0, 14.38, 14.42, 22.2, 24.1, 29.2, 33.2, 121.9, 125.9, 128.2, 128.8, 129.1, 131.9, 133.7, 137.8, 139.0, 143.2, 148.6, 149.5. IR (neat): 3064 m, 3051 m, 2958 s, 2927 s, 2868 s, 1583 m, 1556 w, 1458 m, 1435 s, 1377 w, 1335 w, 1304 w, 1271 w, 1236 w, 1186 w, 1159 w, 1122 w, 1092 m, 1066 w, 1028 w, 999 w, 912 w, 793 s, 766 s, 733 s, 698 s, 673 w, 648 w, 594 m, 484 w, 463 m, 426 w. MS, *m/z* (relative intensity, %): 354 (M^++2, 18), 353 (M^++1, 18) 352 (M^+, 100), 351 (35), 350 (M^+-2, 76), 348 (M^+-4, 55), 339 (13), 338 (12), 337 (82), 336 (26), 335 (58), 333 (43), 310 (14), 309 (50), 308 (22), 307 (40), 305 (26), 295 (19), 293 (16), 291 (11), 279 (17), 277 (13), 245 (12), 243 (11), 233 (17), 231 (17), 229 (19), 226 (21), 219 (13), 217 (12), 215 (13), 205 (14), 203 (20), 202 (12), 191 (36), 189 (18), 185 (20), 167 (62), 166 (20), 165 (60), 163 (35), 157 (32), 155 (20), 153 (25), 151 (75), 150 (16), 149 (57), 147 (42), 143 (37), 142 (19), 141 (34), 129 (53), 128 (50), 115 (67), 105 (20), 91 (77), 89 (75), 88 (11), 87 (54), 85 (39), 77 (13). Exact Mass (EI): Calcd for $C_{21}H_{26}Ge$ 352.1246, found 352.1247.

1-Methyl-1-phenyl-2,3-dipropyl-1*H*-benzo[*b*]silole (23b)



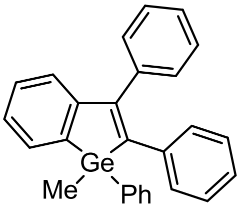
Colorless oil. Rf 0.54 (hexane). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 0.65 (s, 3H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H), 1.37-1.49 (m, 2H), 156-1.65 (m, 2H), 2.29-2.36 (m, 1H), 2.41-2.48 (m, 1H), 2.57-2.61 (m, 2H), 7.14-7.17 (m, 1H), 7.30-7.39 (m, 5H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.49-7.51 (m, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: -5.5, 14.4, 14.5, 22.1, 23.7, 29.1, 32.0, 121.1, 125.8, 127.9, 129.5, 129.8, 131.9, 134.3, 135.1, 137.1, 140.7, 150.9, 152.9. IR (neat): 3064 m, 3051 m, 2958 s, 2929 s, 2868 s, 1583 m, 1552 m, 1460 m, 1433 m, 1377 w, 1304 w, 1273 w, 1250 m, 1190 w, 1163 w, 1130 m, 1109 m, 1061 w, 1030 w, 916 w, 796 s, 768 s, 725 s, 698 s, 476 m, 465 m, 422 m. MS, *m/z* (relative intensity, %): 307 (M^++1, 12), 306 (M^+, 46), 263 (19), 235 (10), 199 (18), 185 (16), 184 (22), 145 (19), 122 (12), 121 (100), 105 (22). Exact Mass (EI): Calcd for $C_{21}H_{26}$GSi 306.1804, found 306.1802.

1,1-Dimethyl-2,3-dipropyl-1*H*-benzo[*b*]silole (24b) [CAS: 1160757-32-3]



Colorless oil. Rf 0.69 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.29 (s, 6H), 0.95-1.03 (m, 6H), 1.49-1.57 (m, 4H), 2.38 (t, *J* = 7.8 Hz, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.26-7.35 (m, 2H), 7.48 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.4, 14.4, 14.6, 22.0, 23.7, 29.0, 31.9, 120.9, 125.5, 129.5, 131.2, 138.4, 142.0, 150.2, 151.0. MS, *m/z* (relative intensity, %): 244 (M^+, 30), 215 (11), 201 (19), 184 (12), 173 (12), 155 (10), 145 (24), 73 (32), 59 (100). Exact Mass (EI): Calcd for found $C_{16}H_{24}$Si 244.1647, found 244.1640.

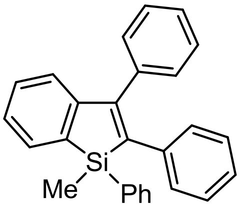
1-Methyl-1,2,3-triphenyl-1*H*-benzo[*b*]germole (25a)



Colorless oil. Rf 0.11 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.97 (s, 3H), 6.94-6.97 (m, 2H), 7.01-7.12 (m, 4H), 7.25-7.33 (m, 4H), 7.34-7.41 (m, 6H), 7.55-7.58 (m, 2H), 7.62-7.64 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -5.0, 125.0, 125.8, 127.0, 127.1, 127.8, 128.4, 128.5, 128.9, 129.2, 129.3, 129.8, 132.2, 133.8, 137.1, 138.5, 138.6, 140.0, 143.1, 150.2, 151.0. IR (neat): 3055 s, 3024 m, 2958 m, 1593 m, 1541 m, 1489 m, 1441 s, 1404 w, 1300 m, 1248 s, 1153 w, 1128 m, 1070 m, 1030 m, 995 m, 910 m, 876 m, 841 s, 800 s, 779 s, 756 s, 727 s, 702 s, 650 m, 611 w, 590 w, 544 w, 490 w, 417 m. MS, *m/z* (relative intensity, %): 422

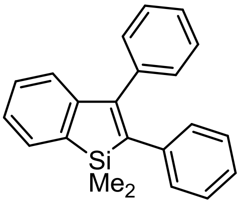
(17), 421 (21), 420 (M^+, 74), 419 (30), 418 (M^+-2, 53), 417 (12), 416 (M^+-4, 38), 407 (23), 406 (27), 405 (100), 404 (40), 403 (75), 402 (17), 401 (56), 330 (20), 329 (11), 254 (21), 253 (46), 252 (79), 250 (15), 227 (19), 226 (13), 225 (17), 223 (11), 153 (12), 151 (56), 150 (16), 149 (42), 147 (33). Exact Mass (EI): Calcd for $C_{27}H_{22}Ge$ 420.0933, found 420.0938.

1-Methyl-1,2,3-triphenyl-1*H*-benzo[*b*]silole (25b)



Colorless oil. Rf 0.11 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.82 (s, 3H), 6.95 (d, *J* = 6.4 Hz, 2H), 7.02-7.10 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.25-7.44 (m, 10H), 7.63 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -5.8, 124.1, 125.7, 126.9, 127.2, 127.8, 128.1, 128.4, 128.8, 129.6, 129.8, 130.0, 132.3, 134.2, 134.5, 136.7, 138.0, 139.5, 141.2, 151.2, 154.4. IR (neat): 3053 s, 3022 s, 2962 m, 1593 s, 1543 m, 1489 s, 1437 s, 1302 s, 1250 s, 1184 m, 1153 m, 1109 s, 1068 s, 1030 m, 993 s, 908 s, 874 m, 810 s, 791 s, 768 s, 733 s, 700 s, 667 m, 615 w, 592 m, 546 w, 488 s, 467 s, 428 m. MS, *m/z* (relative intensity, %): 375 (M^++1, 35), 374 (M^+, 100), 360 (29), 359 (87), 252 (11), 181 (17), 105 (30). Exact Mass (EI): Calcd for $C_{27}H_{22}Si$ 374.1491, found 374.1491.

1,1-Dimethyl-2,3-diphenyl-1*H*-benzo[*b*]silole (26b) [CAS: 1016642-73-1]



White solid. Rf 0.17 (hexane). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.49 (s, 6H), 6.98-7.00 (m, 2H), 7.05-7.09 (m, 2H), 7.14 (t, *J* = 7.6Hz, 2H), 7.20-7.22 (m, 2H), 7.25-7.37 (m, 5H), 7.62-7.64 (m, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: -3.5, 123.9, 125.6, 126.6, 127.0, 127.9, 128.3, 128.6, 129.6, 129.7, 131.6, 138.0, 138.1, 139.9, 142.9, 150.6, 153.0. MS, *m/z* (relative intensity, %): 313 (M^++1, 29), 312 (M^+, 100), 298 (27), 297 (96), 252 (12), 121 (26), 119 (30), 105 (10), 93 (17). Exact Mass (EI): Calcd for $C_{22}H_{20}Si$ 312.1334, found 312.1334.

1.5 References and Notes

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(2) For selected catalytic reactions involving the cleavage of C-Ge bonds, see: (a) Kosugi, M.; Tanji, T.; Tanaka, Y.; Yoshida, A.; Fugami, K.; Kameyama, M.; Migita, T. *J. Organomet. Chem*. **1996**, *508*, 255. (b) Spivey, A. C.; Gripton, C. J. G.; Hannah, J. P.; Tseng, C.-C.; de Fraine, P.; Parr, N. J.; Scicinski, J. J. *Appl. Organomet. Chem*. **2007**, *21*, 572. (c) Pitteloud, J.-P.; Zhang, Z.-T.; Liang, Y.; Cabrera, L.; Wnuk, S. F. *J. Org. Chem*. **2010**, *75*, 8199.

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Chapter 2

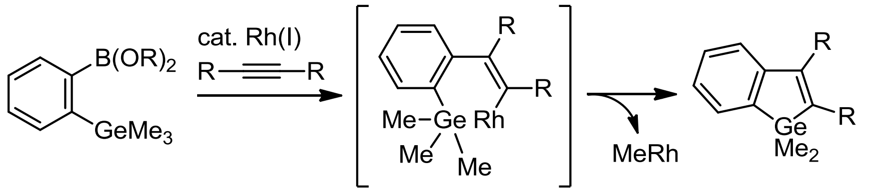
Palladium-Catalyzed Synthesis of Benzofuzed Phosphacycles via Carbon-Phosphorus Bond Cleavage

2.1 Introduction

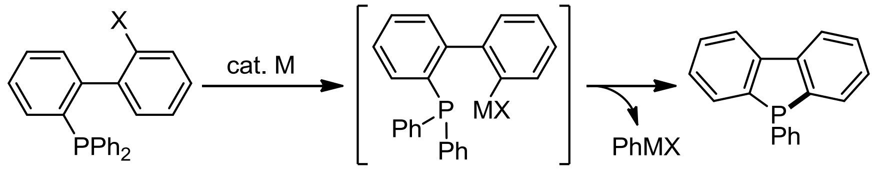
As described in Chapter 1, the catalytic cleavage of C-Ge bond could be achieved by the proximity effect between a rhodium center and a C-Ge bond (Scheme 2.1a). Based on this result, the synthesis of phospholes via the cleavage of C-P bond was next investigated (Scheme 2.1b). Phospholes have recently received considerable attention as promising organic materials because of their characteristic optical and electronic properties, which are derived from the phosphorus-bridged 1,3-dienic π-system.[1] As described in the general introduction, the methods used for the synthesis of phosphole have several limitations, including a low functional group compatibility and the sensitivity of the reagents to air and water. In view of the widespread availability and stability of triarylphosphines, a more synthetically valuable intramolecular cross-coupling reaction using triarylphosphines was examined and the results are reported in Chapter 2.

Scheme 2.1. Catalytic Synthesis of Phospholes through the Cleavage of C-P Bond

(a) the synthesis of germoles through the cleavage of C-Ge bond (Chapter 1)

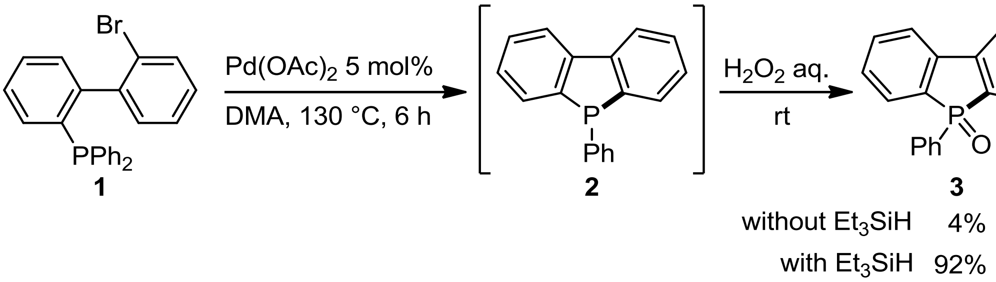


(b) the synthesis of phospholes through the cleavage of C-P bond (Chapter 2)



2.2 Results and Discussion

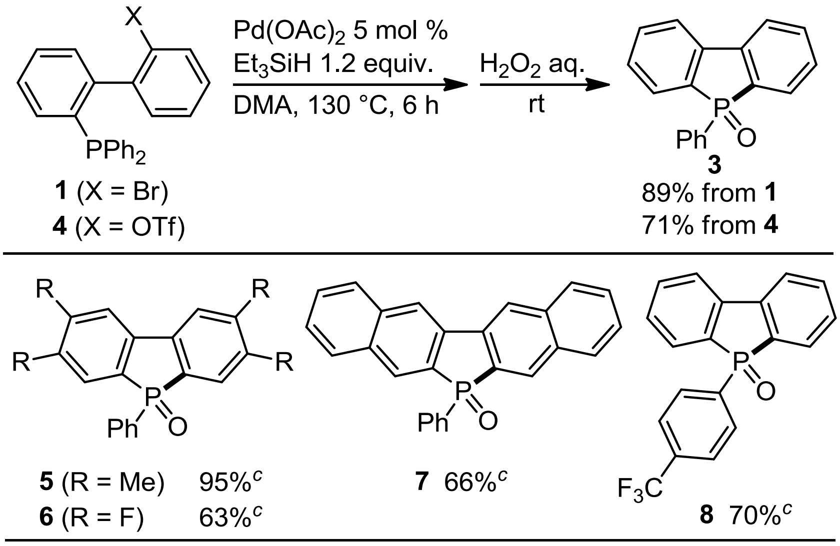
The reaction of 2-bromo-2’-diphenylphosphinobiphenyl (**1**) was initially examined. The expected phosphole was detected in 4% yield using $Pd(OAc)_2$ catalyst (eq 2.1). Since the generated phosphole (**2**) is susceptible to oxidation upon workup, the product was therefore isolated in the form of the corresponding oxide after oxidation by hydrogen peroxide. After numerous optimization studies, we found that the addition of triethylsilane to the reaction mixture dramatically improved yield to 92%.



(2.1)

Scope of substrates is shown in Table 2.1. Both bromides (**1**) and triflates (**4**) served as the appropriate precursors for the palladium-catalyzed cyclization via C-P bond cleavage. A brief survey of several biaryl substrates demonstrated that a series of fused phosphole derivatives could be synthesized in a similar manner.

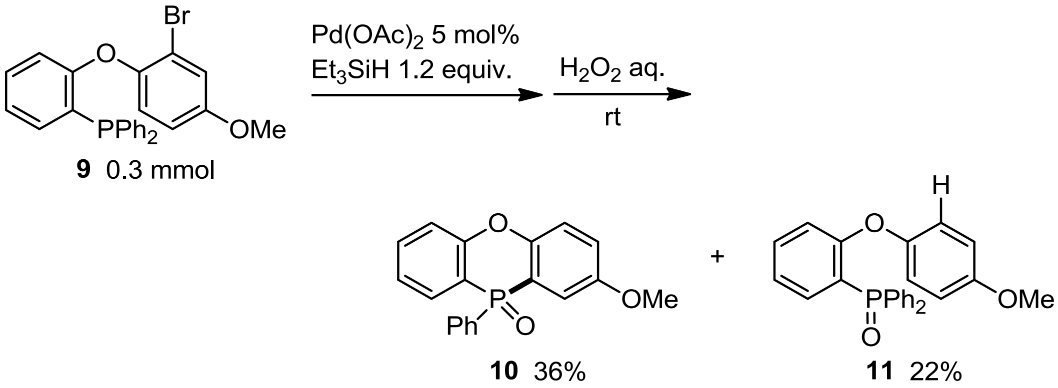
Table 2.1. Palladium-Catalyzed Synthesis of Phosphole Derivatives[a,b]



[a] Reaction conditions: substrate (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), Et_3SiH (0.36 mmol), DMA (0.6 mL), at 130 °C for 6 h. [b] Isolated yield. [c] Corresponding bromides were used as starting materials.

Attempt to synthesis of six-membered phsophacycles, the palladium-catalyzed reaction of phosphine **9** was examined (Scheme 2.2). As a result, the desired product (**10**) was obtained in low yield along with reductive debromination by-product (**11**).

Scheme 2.2. Palladium-Catalyzed Synthesis of Six-Membered Phosphacycles



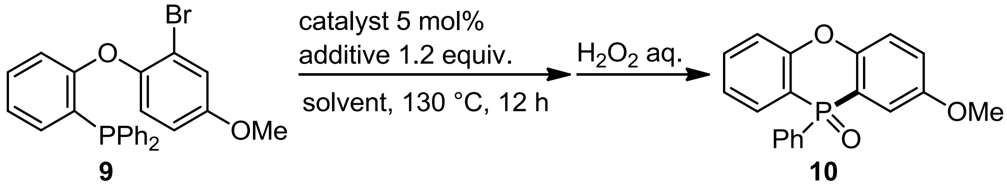
9 0.3 mmol

10 36%

11 22%

After several experiments, the substituents on the silicon atom were found to have a profound impact on the efficiency of the reaction (Table 2.2, entries 3-6). The addition of a bulkier hydrosilane such as $(Me_3Si)_3SiH$ improved the yield, providing 86% of **10** (Table 2.2, entry 6). This catalytic cyclization could also be conducted in non-polar solvents, such as toluene and dioxane, without significant decrease in yield (Table 2.2, entries 7 and 8). Palladium(0) complexes also served as effective catalyst precursors (Table 2.2, entries 9 and 10).

Table 2.2. Palladium-Catalyzed Synthesis of Phosphole Derivatives[a,b]

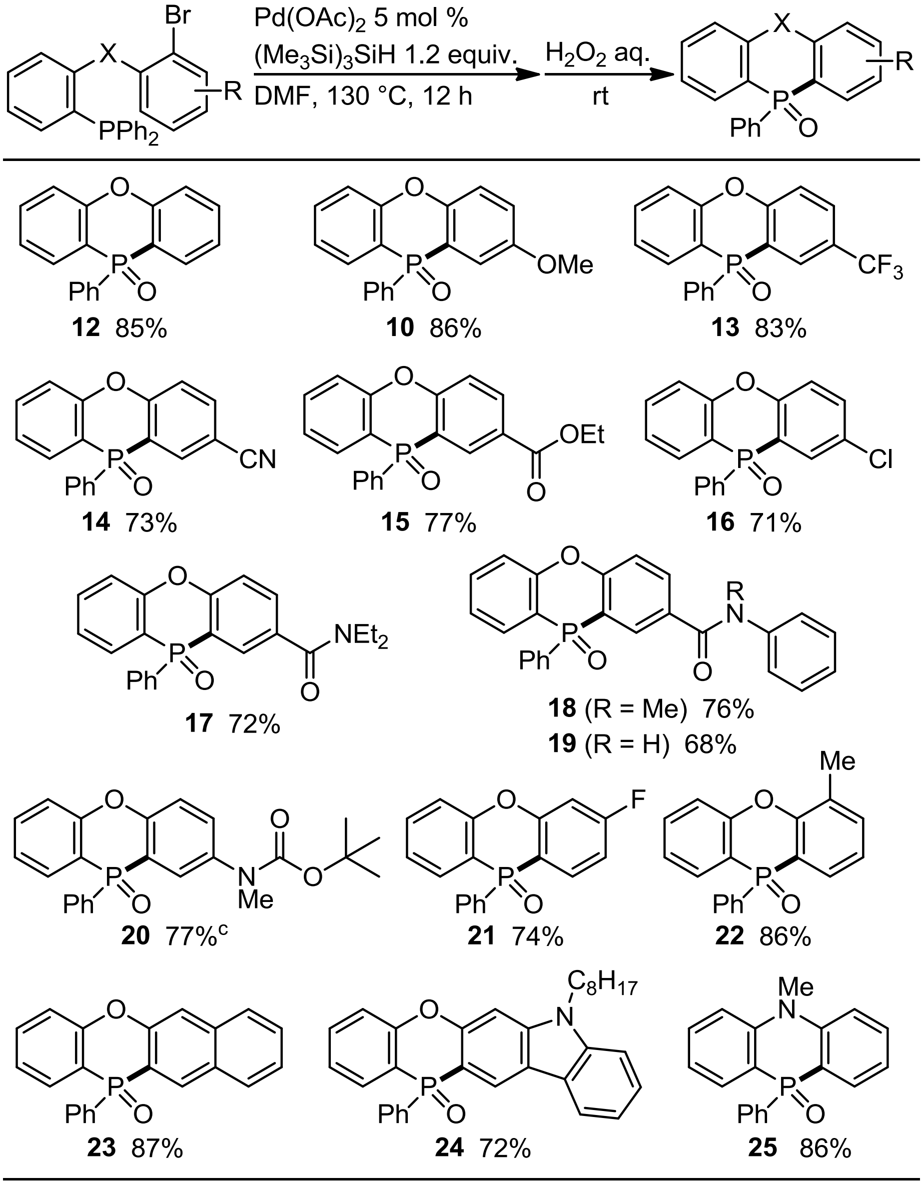


entry	catalyst	additive	solvent	NMR yield
1	$Pd(OAc)_2$	-	DMF	19%
2	$Pd(OAc)_2$	Zn	DMF	56%
3	$Pd(OAc)_2$	$(EtO)_3SiH$	DMF	28%
4	$Pd(OAc)_2$	Et_3SiH	DMF	36%
5	$Pd(OAc)_2$	$^{i}Pr_3SiH$	DMF	53%
6	$Pd(OAc)_2$	$(Me_3Si)_3SiH$	DMF	83% (86%)[b]
7	$Pd(OAc)_2$	$(Me_3Si)_3SiH$	toluene	81%
8	$Pd(OAc)_2$	$(Me_3Si)_3SiH$	1,4-dioxane	76%
9	$Pd_2(dba)_3\cdot CHCl_3$	$(Me_3Si)_3SiH$	DMF	70%
10	$Pd(PPh_3)_4$	$(Me_3Si)_3SiH$	DMF	81%

[a] Reaction conditions: **9** (0.20 mmol), catalyst (0.010 mmol), additive (0.24 mmol), solvent (0.4 mL), for 12 h. [b] Isolated yield.

With optimized reaction conditions in hand, we next examined the scope of substrates for this catalytic cyclization reaction. As depicted in Table 2.3, a wide range of functional groups was tolerated. In particular, phosphacycles containing cyano, ester, amide and carbamate groups (*i.e.*, **14**, **15**, **17-20**), which are inaccessible by the classical method using organlithium reagents, could be synthesized successfully. Our catalytic method also enabled the incorporation of aromatic and heteroaromatic rings other than phenyl, allowing for the synthesis of π-extended phosphacycles, such as those containing naphthalene and carbazole (*i.e.*, **23** and **24**). In addition to the phenoxaphosphinine scaffold, phenophosphazine derivative **25** could also be prepared by using a nitrogen-tethered substrate.

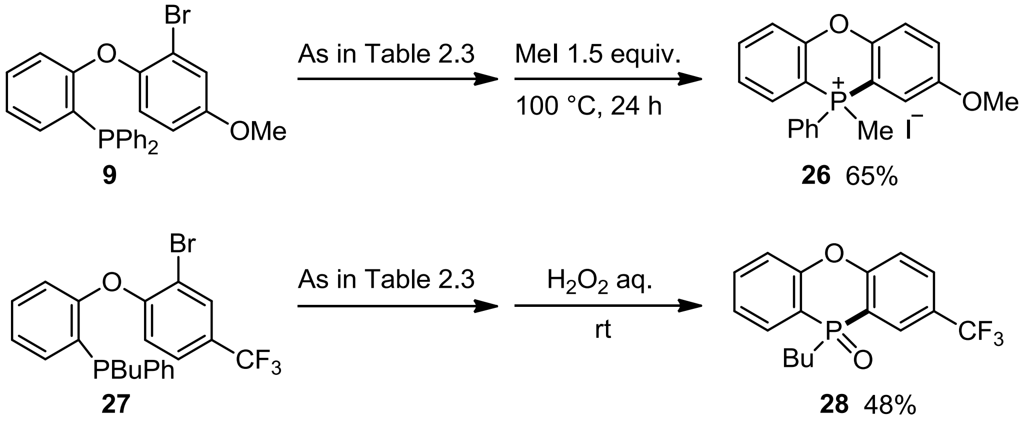
Table 2.3. Palladium-Catalyzed Synthesis of Six-Membered Phosphacycles[a,b]



[a] Reaction conditions: bromide (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), $(Me_3Si)_3SiH$ (0.36 mmol), DMF (0.6 mL), at 130 °C for 12 h. [b] Isolated yield. [c] Substrate (0.30 mmol), $Pd(OAc)_2$ (0.015 mmol), $(Me_3Si)_3SiH$ (0.36 mmol), K_3PO_4 (0.36 mmol), DMF (0.6 mL), at 130 °C for 12 h.

Although we routinely isolated the products as the oxides, the phosphorus center of the resulting phosphacycles can be differently modified through a suitable post-treatment. For example, treatment of phosphacycle **10** (prepared from **9**) with MeI produced the phosphonium salt **26** (Scheme 2.3). When the substrate bearing a PPhBu group, *i.e.*, **27** was exposed to the catalytic conditions, a phenyl group, rather than a butyl group, was eliminated exclusively to deliver a P-alkyl-substituted phosphacycle **28**.

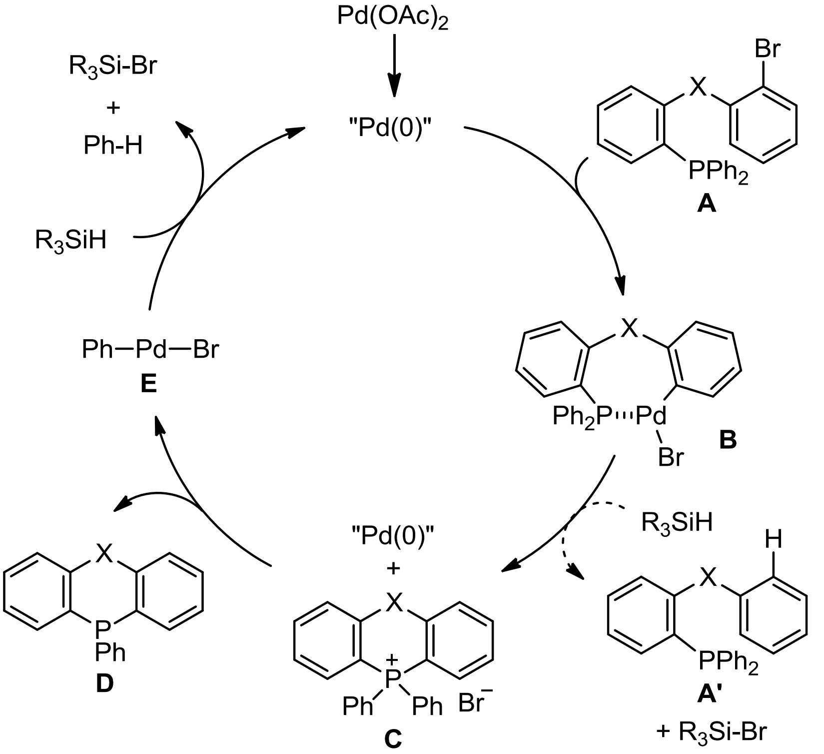
Scheme 2.3. Synthesis of Phosphonium Salt **26** and P-Alkyl Derivative **28**



A possible mechanism for the reaction is depicted in Scheme 2.4. The oxidative addition of bromide **A** to the Pd(0) species initially forms a palladacycle **B**. Subsequent C-P bond-forming reductive elimination from **B** generates a cyclic phosphonium salt **C**, along with a Pd(0) species.[2] The P-Ph bond in the phosphonium **C** can be cleaved through oxidative addition to the Pd(0) species, releasing a phosphacycle product **D** and PhPdBr **E**. If intermediate **E** undergoes reductive elimination of PhBr, an active Pd(0) species can be regenerated. However, such a C-halogen bond forming reductive elimination is known to be thermodynamically unfavorable.[3] Thus, the reaction only proceeded in low yield when the reaction was conducted in the absence of a reducing agent. Addition of hydrosilane can promote the regeneration of Pd(0) by reductively cleaving Pd(II) intermediate **E** to benzene and silyl bromide, similar to the process involved in the catalytic reductive dehalogenation of aryl halides.[4] When less bulky hydrosilanes were used, reductive debromination of **A** occurs competitively to form **A’**, thus resulting in a lower yield of the desired cyclized product **D**.

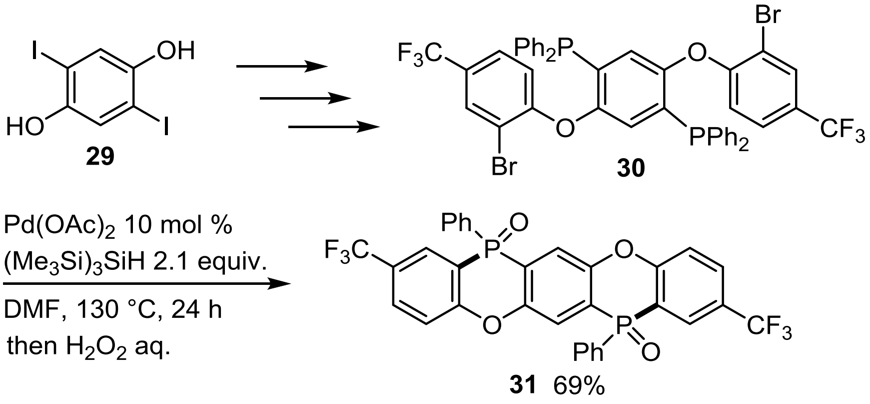
Bulky $(Me_3Si)_3SiH$ effectively discriminates Pd(II) intermediates **B** and **E**, allowing for the exclusive formation of **D**.

Scheme 2.4. A Possible Mechanism



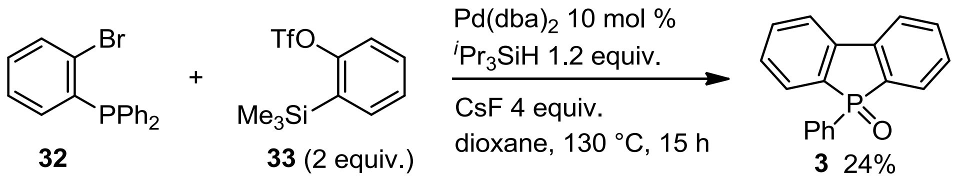
Our method could be useful for the construction of a π-extended ladder-type structure through double cyclization. Bisphosphine **31** prepared from **30** was readily converted to **32** via successive cleavage of C-P bonds (Schem 2.5).

Scheme 2.5. Synthesis of π-Extended Phosphacycle **31**



If the palladacycle intermediate that is capable of undergoing C-P bond cleavage, such as **B** in Scheme 2.4, can be assembled in an intermolecular manner, the utility of the method would be further enhanced. One way to achieve such a goal involves a carbopalladation of bromide **32** across an alkyne, which should eventually lead to the formation of the benzophosphole derivative. A preliminary study revealed that our reaction design could be realized by using a benzyne as the alkyne component. Thus, the palladium-catalyzed reaction of bromide **32** with the benzyne precursor **33** in the presence of CsF and hydrosilane afforded the dibenzophosphole **3** in 24% yield (Scheme 2.6).

Scheme 2.6. Intermolecular Assembly of Dibenzophosphole via Catalytic C-P Bond Cleavage



2.3 Conclusion

In summary, the catalytic method for the synthesis of benzofused phosphacycles was developed. The method features C-P bond cleavage, which allows for the use of tertiary phosphines as a stable and readily available phosphorus source. It proved to be highly compatible with several functional groups including esters, amides, and carbamates. This method overcomes the limitation encountered in the classical method that uses organolithium reagents.

2.4 Experimental Section

General Information.

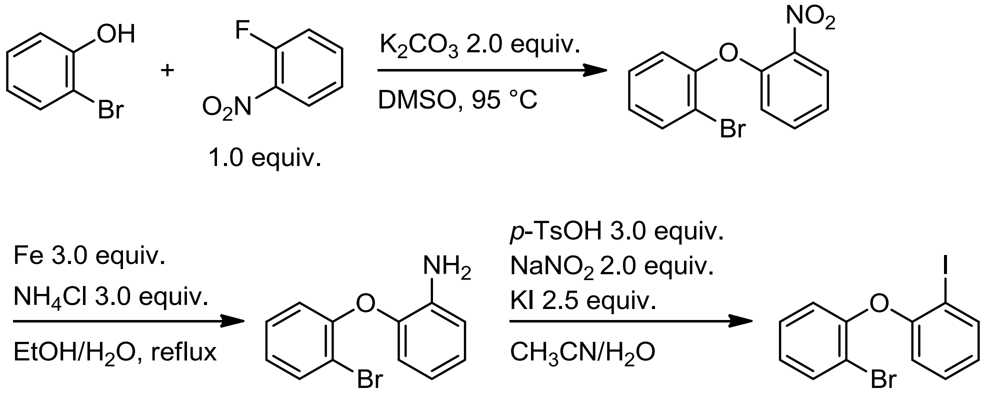
^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMTC-400/54/ss spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{31}P NMR spectra were recorded in $CDCl_3$ with H_3PO_4 as the internal standard using a JEOL ECS-400 spectrometer. Data have been reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, quart = quartet, quint = quintet, m = multiplet and br = broad peak), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a JASCO TF/IR-4000; absorptions have been reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were recorded on a Shimadzu GCMS-QP 2010 instrument with an ionization voltage of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-700 spectrometer. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO_2 [Merck SilicaGel 60 (230-400 mesh) or Silycycle Silica Flash F60 (230-400 mesh)]. Gel permeation chromatography (GPC) was performed using a LC-9210NEXT HPLC or LC9225NEXT HPLC system. All of the reactions were carried out in 10 mL sample vials with Teflon-sealed screw caps.

Materials.

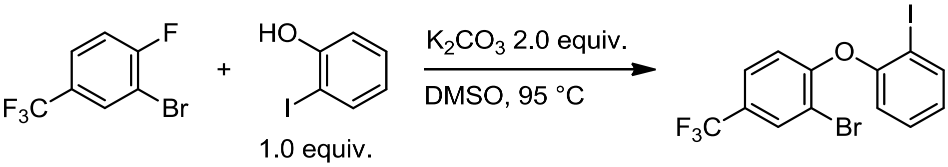
Unless otherwise noted, all reagents were obtained from commercial suppliers and were used as received. $Pd(OAc)_2$ (CAS: 3375-31-3) and 1,4-dioxane (CAS: 123-91-1) was purchased from Wako Pure Chemical Industries, Ltd. $(Me_3Si)_3SiH$ (CAS: 1873-77-4), Et_3SiH (CAS: 617-86-7) (2-bromophenyl)diphenylphosphine (**32**, CAS: 62336-24-7), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**33**, CAS: 88284-48-4), $^iPr_3SiH$ (CAS: 6485-79-6) and CsF (CAS: 13400-13-0) were purchased from Tokyo Chemical Industry Co., Ltd. DMF was dried on a glass contour solvent-dispensing system (Nikko Hansen & Co., Ltd.). 2-Bromo-2'-(diphenylphosphanyl)-1, 1'-biphenyl (**1**, CAS: 202928-34-5) was prepared according to the literature procedure.[5]

Synthesis of the Starting Amides.

Synthesis of 2,2'-Dihalobiaryl

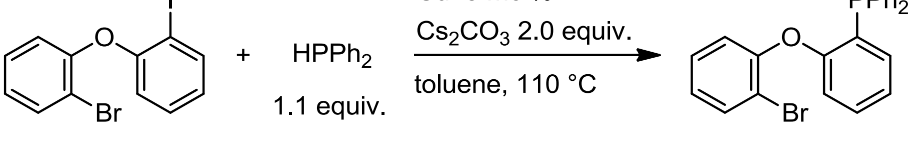


Method A.[6] K_2CO_3 (12 g, 90 mmol) was added to a solution of 2-bromophenol (7.8 g, 45 mmol) and 2-fluoronitrobenzene (6.4 g, 45 mmol) in DMSO (150 mL) and the suspension was stirred at 95 °C overnight. After cooling to room temperature, water (100 mL) was added to the reaction mixture, and the resulting mixture was extracted with EtOAc (3×50 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was then removed under reduced pressure to give 1-bromo-2-(2-nitrophenoxy)benzene [CAS: 60671-89-8] as a white solid (13 g). The crude product was dissolved in EtOH (50 mL) and H_2O (50 mL), and Fe powder (7.5 g, 135 mmol) and NH_4Cl (7.2 g, 135 mmol) were then added. The reaction mixture was refluxed for 3 h. After cooling to room temperature, the mixture was filtered through a pad of Celite and concentrated in vacuo. To the residue was added brine (100 mL) and then it was extracted with EtOAc (3×50mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the aniline derivative as a brown solid (12 g). This product was used to next step without further purification. To a solution of the brown solid (12 g) in acetonitrile (180 mL) was added *p*-TsOH·H_2O (26 g, 135 mmol). After cooling to 0 °C, a solution of $NaNO_2$ (6.2 g, 90 mmol) and KI (19 g, 113 mmol) in H_2O (90 mL) was added dropwise and it was stirred at room temperature overnight. The reaction was quenched by addition of saturated aqueous solution of $NaHCO_3$ (30 mL). Following the extraction with EtOAc (3×50 mL) the organic phase was washed with $Na_2S_2O_3$ aq. (30 mL) and dried over $MgSO_4$. The solvent was then removed in vacuo to give the crude product. The crude product was purified by column chromatography (hexane) to give 2-bromo-1-2-iodophenoxybenzene as a colorless oil (11 g, 30 mmol) in 67% yield over three steps.



Method B.[6] K_2CO_3 (5.7 g, 41 mmol) was added to a solution of 2-iodophenol (4.5 g, 21 mmol) and 2-bromo-1-fluoro-4-(trifluormethyl)benzene (5.0 g, 21 mmol, purchased from TCI) in DMSO (65 mL) and the suspension was stirred at 95 °C for 48 h, and then the reaction mixture was poured into water (100 mL). After the extraction with EtOAc (3×30 mL) and drying over $MgSO_4$ the solvent was removed in vacuo. The crude product was then purified by column chromatography (Hexane/EtOAc) to afford the desired product as a colorless oil (8.3 g, 19 mmol, 91%).

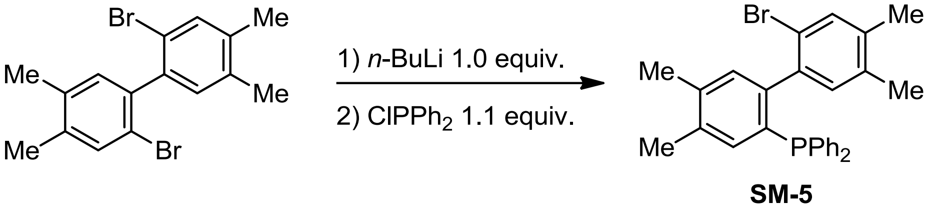
Phosphination



SM-12

Method C.[7] A two-necked flask was charged with 1-bromo-2-(2-iodophenoxy)benzene (5.6 g, 15 mmol, synthesized by Method A), diphenylphosphine (3.1 g, 17 mmol), CuI (0.14 g, 0.75

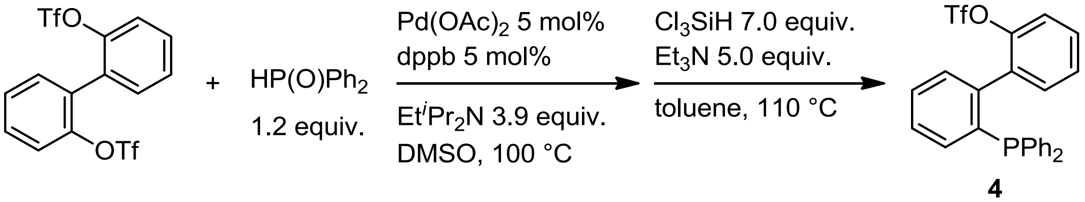
mmol), Cs_2CO_3 (9.8 g, 30 mmol) and dry toluene (45 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 48 h and cooled to room temperature. The mixture was filtered through a pad of Celite and evaporated in vacuo to give the crude product. Purification by flash chromatography (hexane/EtOAc) and GPC gave (2-(2-bromophenoxy)phenyl)diphenylphosphine as a white solid (**SM-12**, 3.2 g, 50%).



SM-5

Method D.[5] A two-necked flask was charged with 2,2'-dibromo-4,4',5,5'-tetramethyl-1,1'-biphenyl[8] (1.5 g, 4.0 mmol) in dry THF (25 mL) and cooled to -110 °C. *n*-BuLi (1.6 M in hexane, 2.5 mL, 4.0 mmol) was added dropwise to the mixture and stirred for 30 min. Then, a solution of $ClPPh_2$ (0.97 g, 4.4 mmol) in THF (4.0 mL) was added dropwise and the reaction mixture stirred for 1 h. The reaction mixture was allowed to warm to room temperature overnight. Then, 1 M HCl aq. (20 mL) was added to the solution and it was extracted with EtOAc (3×20 mL). The combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by flash chromatography (hexane/EtOAc) gave **SM-5** (1.3 g, 67%) as a white solid.

2'-(Diphenylphosphino)-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate [CAS: 189445-84-9] (4).

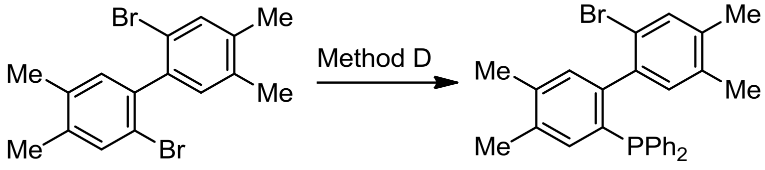


4

2,2'-Biphenylylene ditriflate[9] (4.4 g, 9.8 mmol), $Pd(OAc)_2$ (0.11 g, 0.50 mmol), dppb (0.21 g, 0.50 mmol), and diphenylphosphine oxide (2.3 g, 12 mmol) were added to a two-neck flask under nitrogen. To this flask were added dry DMSO (50 mL) and $Et^{i}Pr_2N$ (6.6 mL, 38 mmol). The reaction mixture was heated to 100 °C overnight. The reaction mixture was diluted with CH_2Cl_2 and washed subsequently with 1 M HCl aq. (30 mL), sat. $NaHCO_3$ aq. (30 mL), and brine (30 mL). The organic solution was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc) to afford 2'-(diphenylphosphoryl)-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3.9 g, 7.7 mmol). $HSiCl_3$ (1.0 mL, 10 mmol) was added to a solution of the product (1.0 g, 2.0 mmol) and Et_3N (2.0 mL, 14 mmol) in dry toluene (50 mL) under nitrogen atmosphere, and the mixture was heated under reflux overnight. After cooling to room temperature, sat. $NaHCO_3$ aq. (2 mL) was added and the solution was further stirred for 5 min. This mixture was filtered through a pad of alumina and evaporated in vacuo to give a crude product. The residue was purified by flash chromatography (EtOAc/hexane = 10/1) to afford **4** as a white solid.

White solid (0.47g, 48%). Mp = 117 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^1H NMR ($CDCl_3$, 399.78 MHz) δ: 7.02 (d, *J* = 7.2 Hz, 1H), 7.10-7.21 (m, 6H), 7.28-7.7.44 (m, 11H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 118.3 (q, *J* = 320.3 Hz), 121.2, 123.1, 127.5, 128.3, 128.4 (d, *J* = 1.9 Hz), 128.4, 128.7, 129.5, 130.6 (d, *J* = 5.8 Hz), 132.8 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 20.1 Hz), 133.8 (d, *J* = 20.1 Hz), 133.9, 135.1 (d, *J* = 6.7 Hz), 136.617, 136.622 (d, *J* = 23.9 Hz), 137.3 (d, *J* = 13.5 Hz), 140.8, 141.1, 146.5. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -12.7. IR (ATR): 1461 w, 1434 w, 1416 s, 1246 w, 1202 s, 1142 s, 1100 m, 1071 w, 1028 w, 891 s, 785 m, 767 s, 745 s, 723 m, 696 s. MS m/z (% relative intensity): 488 (28), 487 (M^++1, 100), 337 (26), 277 (17), 262 (12), 261 (63), 260 (12). HRMS (CI): Calcd for $C_{25}H_{19}F_3O_3PS$ 487.0745, Found 487.0748.

(2'-Bromo-4,4',5,5'-tetramethyl-[1,1'-biphenyl]-2-yl)diphenylphosphine (SM-5).

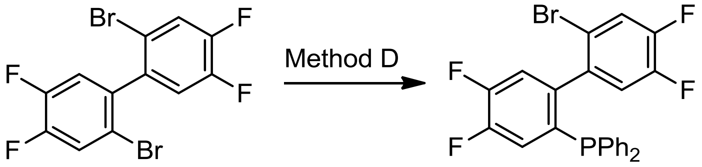


SM-5

This compound was synthesized from 2,2'-dibromo-4,4',5,5'-tetramethyl-1,1'-biphenyl using Method D.

White solid (1.3 g, 67%). Mp = 204 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.96 (s, 3H), 2.17 (s, 3H), 2.22 (s, 3H), 2.27 (s, 3H), 6.59 (s, 1H), 6.86 (d, J = 1.0 Hz, 1H), 6.99 (d, J = 1.0 Hz, 1H), 7.18-7.28 (m, 10H), 7.38 (s, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 19.0, 19.3, 19.67, 19.69, 120.4, 128.0, 128.08, 128.14, 128.2, 131.2 (d, J = 6.6 Hz), 132.8, 133.1 (d, J = 2.9 Hz), 133.3 (d, J = 10.6 Hz), 133.4, 133.6, 133.8 (d, J = 20.1 Hz), 134.7, 136.2, 137.5 (d, J = 5.7 Hz), 137.6 (d, J = 11.5 Hz), 137.9 (J, J = 11.5 Hz), 139.3 (d, J = 6.7 Hz), 144.7, 145.0. ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -14.0. IR (ATR): 2965 w, 1585 w, 1473 w, 1434 m, 1376 w, 1258 w, 1157 w, 1101 w, 1021 w, 995 w, 882 m, 742 m, 695 s. MS m/z (% relative intensity, CI): 476 (30), 475 (M$^+$+3, 99), 474 (31), 473 (M$^+$+1, 100), 395 (12), 394 (28), 393 (89), 317 (40), 316 (18). HRMS (CI): Calcd for C$_{28}$H$_{27}$BrP 473.1034, Found 473.1029.

(2'-Bromo-4,4',5,5'-tetrafluoro-[1,1'-biphenyl]-2-yl)diphenylphosphine (SM-6).

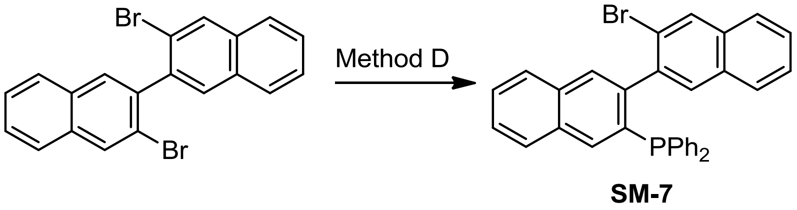


SM-6

This compound was synthesized from 2,2'-dibromo-4,4',5,5'-tetrafluoro-1,1'-biphenyl using Method D.

White solid (1.0 g, 41%). Mp = 114 °C. Rf 0.43 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 6.67 (dd, *J* = 10.2, 8.6 Hz, 1H), 6.87 (t, *J* = 9.5 Hz, 1H), 6.98-7.03 (m, 1H), 7.15-7.23 (m, 4H), 7.30-7.43 (m, 7H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 117.8, 119.2 (dd, *J* = 16.7, 5.3 Hz), 120.3 (dd, *J* = 18.2, 2.8 Hz), 121.4 (d, *J* = 20.2 Hz), 122.2 (d, *J* = 17.3 Hz), 128.69, 128.70 (d, *J* = 13.4 Hz), 129.0, 129.3, 133.5 (d, *J* = 20.1 Hz), 133.9 (d, *J* = 21.1 Hz), 135.1 (d, *J* = 14.4 Hz), 135.2 (d, *J* = 10.6 Hz), 135.5 (d, *J* = 11.5 Hz), 136.5 (d, *J* = 4.7 Hz), 141.2 (d, *J* = 31.7 Hz), 148.7 (dd, *J* = 251.0, 12.5 Hz), 149.7 (dd, *J* = 254.4, 12.9 Hz), 150.19 (dd, *J* = 261.1, 20.6 Hz), 150.24 (dd, *J* = 255.8, 15.3 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -13.0. IR (ATR): 1596 m, 1502 m, 1475 s, 1435 m, 1402 m, 1369 w, 1309 w, 1273 s, 1227 w, 1179 m, 1158 m, 1092 w, 1071 w, 999 w, 894 m, 881 m, 848 w, 798 w, 781 s, 748 s, 724 m, 692 s. MS m/z (% relative intensity, CI): 491 (M^++3, 16), 489 (M^++1, 16), 411 (10), 409 (12), 389 (13), 375 (10), 335 (11), 334 (21), 333 (100), 332 (24), 297 (31), 255 (11). HRMS (CI): Calcd for $C_{24}H_{15}BrF_4P$ 489.0031, Found 489.0026.

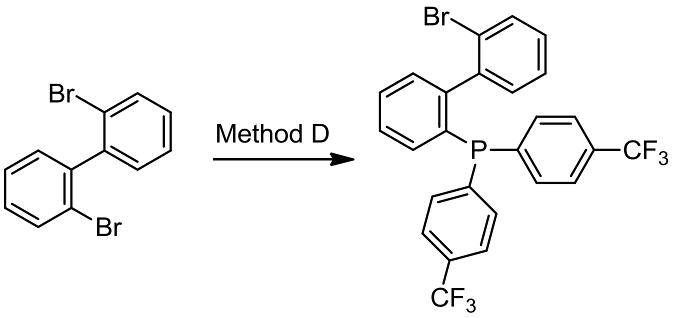
(3'-Bromo-[2,2'-binaphthalen]-3-yl)diphenylphosphine (SM-7).



This compound was synthesized from 3,3'-dibromo-2,2'-binaphthyl using Method D.

White solid (0.50 g, 39%). Mp = 158 °C. Rf 0.34 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.11 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.23 (s, 1H), 7.25-7.32 (m, 6H), 7.36-7.49 (m, 5H), 7.58 (d, *J* = 4.0 Hz, 1H), 7.67-7.74 (m, 3H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 122.5 (d, *J* = 1.9 Hz), 126.2, 126.3, 126.6, 126.8 (d, *J* = 17.3 Hz), 127.7 (d, *J* = 9.6 Hz), 128.0, 128.2 (d, *J* = 7.6 Hz), 128.3 (d, *J* = 6.7 Hz), 128.4, 128.7, 129.0 (d, *J* = 5.7 Hz), 130.6, 131.2 , (d, *J* = 2.8 Hz), 131.5, 132.8, 133.1, 133.5, 133.7, 133.8, 135.3 (d, *J* = 21.1 Hz), 136.1, 136.3, 136.4, 136.8 (d, *J* = 11.6 Hz), 138.8 (d, *J* = 5.7 Hz), 142.8, 143.1. ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -11.2. IR (ATR): 1582 w, 1486 w, 1433 w, 1307 w, 1262 w, 1183 w, 1133 w, 1073 w, 1022 w, 1001 w, 945 w, 887 w, 873 w, 848 w, 807 w, 742 s, 696 s. MS m/z (% relative intensity, CI): 520 (16), 519 (M$^+$+3, 51), 518 (19), 517 (M$^+$+1, 50), 440 (11), 439 (33), 438 (21), 437 (38), 362 (29), 361 (100), 360 (22). HRMS (CI): Calcd for C$_{32}$H$_{23}$BrP 517.0721, Found 517.0715.

(2'-Bromo-[1,1'-biphenyl]-2-yl)bis(4-(trifluoromethyl)phenyl)phosphine (SM-8).

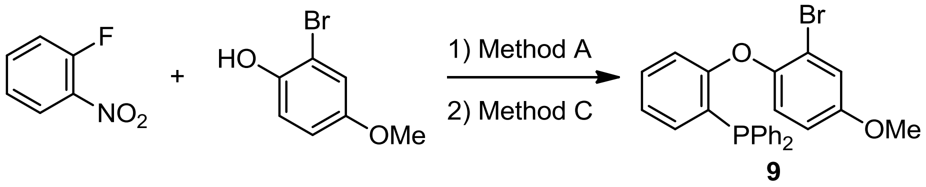


SM-8

This compound was synthesized from 2,2'-dibromo-1,1'-binaphthyl and bis[4-(trifluoromethyl)pheny]chlorophosphine[10] using Method D.

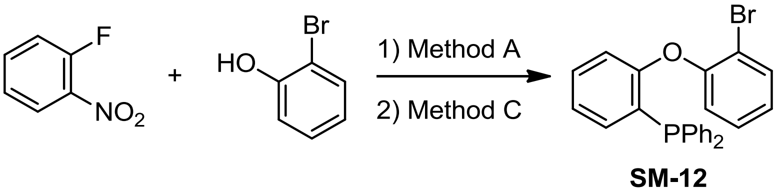
White solid (0.79 g, 48%). Mp = 115 °C. Rf 0.40 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 6.97 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.09 (dd, *J* = 7.6, 4.0 Hz, 1H), 7.15-7.21 (m, 2H), 7.25-7.30 (m, 3H), 7.32-7.39 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.53-7.56 (m, 4H), 7.62 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 123.92 (quart, *J* = 272.1 Hz), 123.94, 123.97 (quart, *J* = 272.1 Hz), 125.0-125.3 (m), 126.7, 128.5, 129.3, 129.6, 130.2 (d, *J* = 5.8 Hz), 130.6 (quart, *J* = 32.6 Hz), 130.9 (quart, *J* = 32.6 Hz), 131.5 (d, *J* = 2.8 Hz), 132.5, 133.6 (d, *J* = 19.1 Hz), 133.8, 133.9 (d, *J* = 21.1 Hz), 134.7 (d, *J* = 10.6 Hz), 141.2 (d, *J* = 15.3 Hz), 141.6 (d, *J* = 8.6 Hz), 141.7, 147.3, 147.6. ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -13.0. IR (ATR): 1396 w, 1320 s, 1163 m, 1118 s, 1059 s, 1015 m, 832 m, 753 m, 699 m. MS m/z (% relative intensity, CI): 556 (14), 555 (M$^+$+3, 49), 554 (15), 553 (M$^+$+1, 51), 489 (21), 483 (37), 475 (10), 473 (28), 385 (10), 371 (10), 330 (20), 329 (100), 328 (20). HRMS (CI): Calcd for $C_{26}H_{17}BrF_6P$ 533.0155, Found 533.0157.

(2-(2-Bromo-4-methoxyphenoxy)phenyl)diphenylphosphine (9).



This compound was synthesized from 1-fluoro-2-nitrobenzene and 2-bromo-4-methoxyphenol (purchased from TCI) using Method A and Method C. White solid (1.3 g, 20%). Mp = 142 °C. Rf 0.29 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.75 (s, 3H), 6.56 (dd, *J* = 7.8, 4.2 Hz, 1H), 6.718 (s, 1H), 6.721 (d, *J* = 2.8 Hz , 1H), 6.83 (ddd, *J* = 7.5, 4.7, 1.7 Hz, 1H), 6.95 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.33-7.41 (m, 10H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.8, 114.4, 114.6, 116.2, 118.2, 122.3, 122.7, 126.9 (d, *J* = 14.4 Hz), 128.3 (d, *J* = 6.7 Hz), 128.6, 130.1, 134.0, 134.2, 136.2 (d, *J* = 10.6 Hz), 146.2, 156.5, 159.4 (d, *J* = 16.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 3061 w, 3006 w, 2972 w, 2939 w, 1599 w, 1486 m, 1462 m, 1433 s, 1288 w, 1255 m, 1210 s, 1181 w, 1159 w, 1127 w, 1093 w, 1065 w, 1037 m, 852 m, 835 m, 816 w, 765 m, 743 s, 694 s. MS m/z (% relative intensity, CI): 466 (25), 465 (M^++3, 96), 464 (30), 463 (M^++1, 93), 386 (12), 385 (46), 384 (21), 383 (45), 363 (10), 308 (20), 307 (100), 306 (27). HRMS (CI): Calcd for $C_{25}H_{21}BrO_2P$ 463.0463, Found 463.0461.

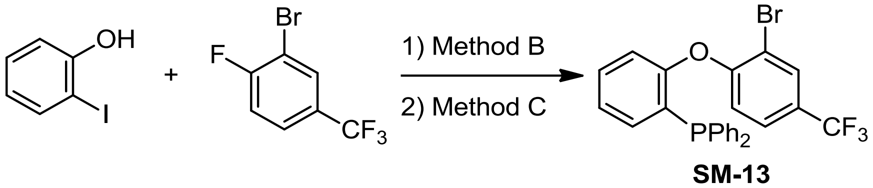
(2-(2-Bromophenoxy)phenyl)diphenylphosphine (SM-12).



SM-12

This compound was synthesized from 1-fluoro-2-nitrobenzene and 2-bromophenol using Method A and Method C. White solid (3.2 g, 50%). Mp = 105 °C. Rf 0.40 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.69 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.87 (t, *J* = 6.0 Hz, 1H), 6.93 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.24-7.37 (m, 11H), 7.52 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.0, 116.5, 120.3, 123.6, 124.9, 128.3, 128.4, 128.7, 130.1, 133.6, 134.0, 134.1, 134.2, 136.0 (d, *J* = 10.6 Hz), 153.0, 158.4 (d, *J* = 16.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -15.9. IR (ATR): 1566 w, 1463 m, 1433 m, 1258 w, 1225 m, 1161 w, 1125 w, 1095 w, 1067 w, 1043 w, 1027 w, 874 w, 794 w, 747 s, 721 w, 695 s, 656 w. MS m/z (% relative intensity, CI): 436 (25), 435 (M^++3, 98), 434 (26), 433 (M^++1, 100), 355 (11), 354 (17), 353 (59), 277 (40), 276 (21). HRMS (CI): Calcd for $C_{24}H_{19}BrOP$ 433.0357, Found 433.0360.

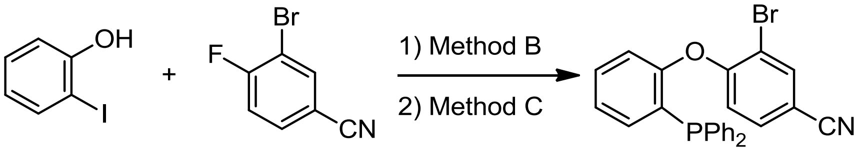
(2-(2-Bromo-4-(trifluoromethyl)phenoxy)phenyl)diphenylphosphine (SM-13).



SM-13

This compound was synthesized from 2-iodophenol and 2-bromo-1-fluoro-4-(trifluormethyl)benzene (purchased from TCI) using Method B and Method C. White solid (0.52 g, 6%). Mp = 119 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.60 (d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 8.0, 3.8 Hz, 1H), 6.96 (ddd, *J* = 7.6, 4.2, 1.8 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.23-7.35 (m, 12H), 7.76 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 113.5, 117.4, 119.2, 123.2 (quart, *J* = 272.1 Hz), 125.2, (quart, *J* = 3.5 Hz), 125.9 (quart, *J* = 33.6 Hz), 128.4 (d, *J* = 6.7 Hz), 128.9, 130.43 (d, *J* = 17.2 Hz), 130.44, 130.8 (quart, *J* = 3.8 Hz), 134.1 (d, *J* = 20.1 Hz), 134.4 (d, *J* = 1.9 Hz), 135.4 (d, *J* = 10.6 Hz), 156.5, 156.7 (d, *J* = 16.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.1. IR (ATR): 1607 w, 1493 w, 1461 m, 1436 m, 1402 w, 1321 s, 1262 s, 1197 w, 1169 m, 1119 s, 1076 s, 1043 m, 999 w, 969 w, 887 m, 819 m, 776 m, 744 s, 694 s. MS m/z (% relative intensity, CI): 503 (M^++3, 22), 501 (M^++1, 21), 423 (12), 421 (12), 401 (11), 346 (21), 345 (100), 344 (23), 303 (36), 267 (16), 219 (11). HRMS (CI): Calcd for $C_{25}H_{18}BrF_3OP$ 501.0231, Found 501.0238.

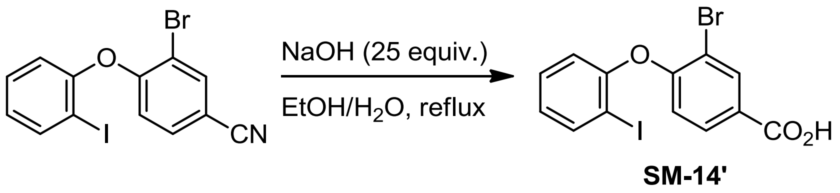
(2-(2-Bromo-4-cyanophenoxy)phenyl)diphenylphosphine (SM-14).



SM-14

This compound was synthesized from 2-iodophenol and 2-bromo-1-fluoro-4-cyanobenzene (purchased from TCI) using Method B and Method C. White solid (075 g, 14%). Mp = 142 °C. Rf 0.20 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.55 (d, *J* = 8.4 Hz, 1H), 6.94-7.00 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.28-7.32 (m, 11H), 7.39 (td, *J* = 7.7, 1.6 Hz, 1H), 7.79 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 106.8, 113.2, 116.7, 117.5, 120.2, 125.9, 128.5 (d, *J* = 7.7 Hz), 129.0, 130.6, 131.1 (d, *J* = 17.2 Hz), 132.3, 134.0 (d, *J* = 20.1 Hz), 134.6 (d, *J* = 1.9 Hz), 135.1 (d, *J* = 10.6 Hz), 137.0, 155.9 (d, *J* = 17.3 Hz), 157.8. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.2. IR (ATR): 2228 w, 1594 w, 1566 w, 1478 m, 1462 m, 1434 m, 1253 s, 1241 s, 1192 m, 1065 w, 1044 w, 892 m, 834 w, 776 m, 744 s, 694 s. MS m/z (% relative intensity, CI): 460 (M^++3, 10), 458 (M^++1, 9), 381 (11), 380 (44), 358 (12), 303 (21), 302 (100), 301 (12). HRMS (CI): Calcd for $C_{25}H_{18}BrNOP$ 458.0309, Found 458.0303.

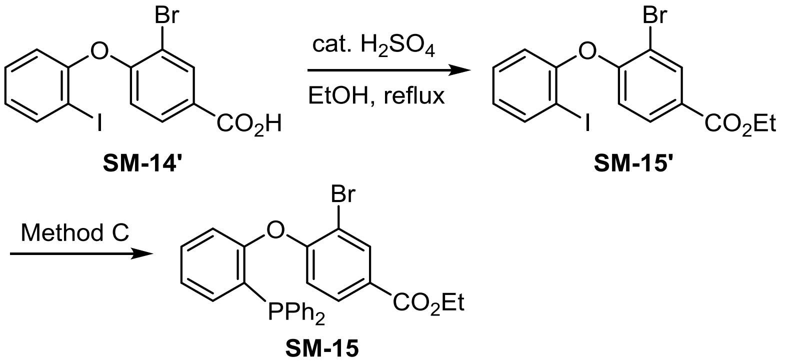
3-Bromo-4-(2-iodophenoxy)benzoic acid (SM-14’)



To a solution of 3-bromo-4-(2-iodophenoxy)benzonitrile (13 g, 33 mmol) in ethanol (120 mL)/H_2O (60 mL) was added sodium hydroxide (33 g, 0.83 mol). The solution was refluxed overnight, and then cooled to room temperature and the ethanol was evaporated. The aqueous layer was cooled to 0 °C, and acidified with concentrated HCl aq. The generated white solid was filtered, washed with water, and dried in vacuo to give **SM-14’** as a white solid (14 g, 33 mmol, 99%).

^{1}H NMR (DMSO-d_6, 399.78 MHz) δ: 6.75 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 7.6 Hz, 2H), 7.46 (t, J = 7.7 Hz, 1H), 7.88 (dd, J = 8.8, 1.6 Hz, 1H), 7.96 (dd, J = 8.0, 1.4 Hz, 1H), 8.21 (d, J = 2.4 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100.53 MHz) δ: 90.3, 112.4, 117.6, 120.9, 127.5, 130.4, 130.87, 130.91, 135.0, 140.5, 154.9, 156.1, 166.7. IR (ATR): 2854 w, 1688 s, 1597 m, 1574 w, 1460 m, 1421 m, 1393 m, 1286 m, 1250 s, 1203 m, 1097 m, 1042 m, 1019 m, 930 w, 892 m, 824 w, 784 m, 762 s, 747 s, 680 m. MS m/z (% relative intensity): 421 (14), 420, (98), 419 (14), 418 (M^+, 100), 294 (12), 292 (13), 212 (66), 195 (30), 169 (19), 168 (51), 167 (11), 139 (24), 76 (16). HRMS (EI): Calcd for $C_{13}H_8BrIO_3$ 417.8701, Found 417.8699.

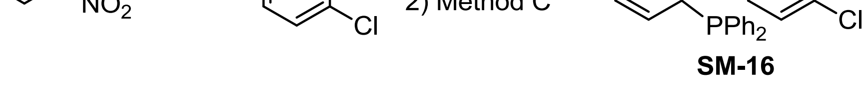
Ethyl 3-bromo-4-(2-(diphenylphosphino)phenoxy)benzoate (SM-15).



A few drops of concentrated H_2SO_4 was added to a solution of **SM-14'** (5.3 g, 13 mmol) in ethanol (160 mL), and the resulting mixture was refluxed for 24 h. After the solvent was evaporated in vacuo, the residue was basified with sat. $NaHCO_3$ aq. until the pH of the solution becomes ~8. The mixture was then extracted with Et_2O (3×30 mL), and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated in vacuo to give **SM-15'** as a pale yellow solid (5.0 g, 88%). **SM-15** was prepared from **SM-15'** using Method C.

Viscous colorless oil (1.2 g, 21%). Rf 0.29 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.37 (t, *J* = 7.2 Hz, 3H), 7.34 (quart, *J* = 6.9 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.87 (dd, *J* = 6.8, 4.0 Hz, 1H), 6.94 (ddd, *J* = 7.7, 4.5, 1.3 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.28-7.35 (m, 11H), 7.74 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.20 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 14.3, 61.1, 113.1, 117.1, 119.1, 125.0, 126.1, 128.4 (d, *J* = 6.7 Hz), 128.8, 129.8, 130.2 (d, *J* = 16.3 Hz), 130.4, 134.0 (d, *J* = 21.0 Hz), 134.4 (d, *J* = 1.9 Hz), 135.0, 135.5 (d, *J* = 10.6 Hz), 156.9 (d, *J* =16.3 Hz), 157.4, 164.9. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 1714 m, 1597 w, 1568 w, 1483 w, 1462 m, 1435 m, 1391 w, 1366 w, 1248 s, 1193 m, 1107 m, 1066 w, 1043 w, 1023 w, 906 m, 871 w, 731 s, 694 s. MS m/z (% relative intensity, CI): 508 (13), 507 (M^++3, 40), 506 (12), 505 (M^+, 40), 428 (29), 427 (100), 426 (19), 425 (19), 350 (14), 349 (59), 348 (11). HRMS (CI): Calcd for $C_{27}H_{23}BrO_3P$ 505.0568, Found 505.572.

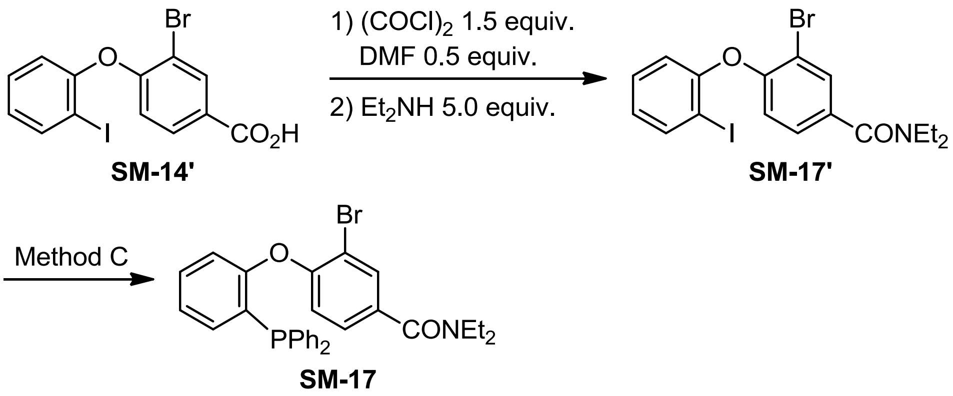
(2-(2-Bromo-4-chlorophenoxy)phenyl)diphenylphosphine (SM-16).



This compound was synthesized from 1-fluoro-2-nitrobenzene and 2-bromo-4-chlorophenol (purchased from TCI) using Method A and Method C.

White solid (2.9 g, 73%). Mp = 88 °C. Rf 0.49 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.58 (d, *J* = 8.8 Hz, 1H), 6.72 (dd, *J* = 7.8, 4.6 Hz, 1H), 6.89 (ddd, *J* = 7.7, 4.5, 1.7 Hz, 1H), 7.02-7.08 (m, 2H), 7.26-7.37 (m, 11H), 7.51 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.1, 117.1, 120.3, 124.1, 128.37, 128.41 (d, *J* = 6.6 Hz), 128.8, 128.9 (d, *J* = 14.4 Hz), 129.0, 130.3, 133.0, 134.1 (d, *J* = 21.1 Hz), 134.3 (d, *J* = 1.9 Hz), 135.8 (d, *J* = 10.5 Hz), 152.2, 157.9 (d, *J* = 16.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 1566 w, 1460 m, 1433 m, 1252 m, 1229 s, 1094 m, 1065 w, 865 w, 831 w, 797 w, 742 s, 695 s. MS m/z (% relative intensity, CI): 469 (M^++3, 19), 467 (M^++1, 14), 391 (34), 390 (29), 389 (100), 388 (20), 387 (13), 313 (14), 312 (11), 311 (40). HRMS (CI): Calcd for $C_{24}H_{18}BrClOP$ 466.9967, Found 466.9964.

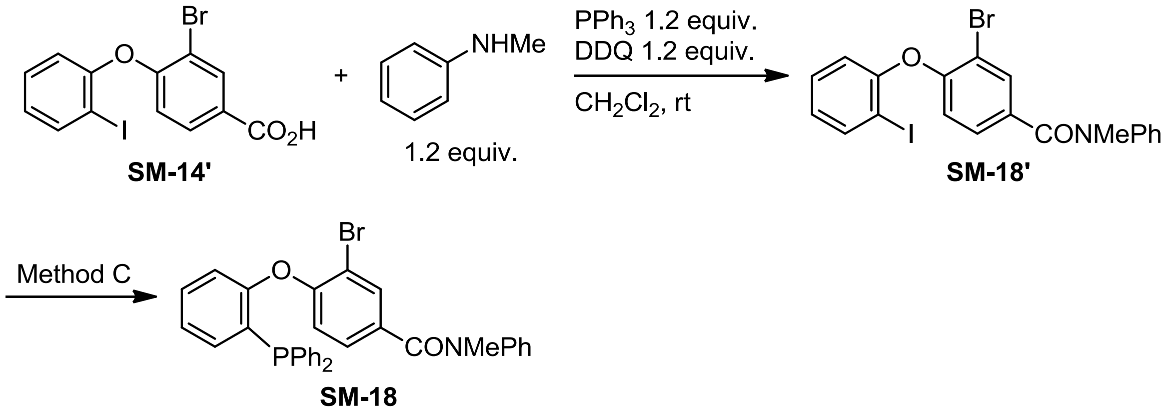
3-Bromo-4-(2-(diphenylphosphino)phenoxy)-*N*,*N*-diethylbenzamide (SM-17).



To a solution of **SM-14’** (5.3 g, 13 mmol) and DMF (0.50 mL, 6.3 mmol) in dry CH_2Cl_2 (30 mL) was added oxalyl chloride (1.6 mL, 19 mmol) dropwise at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 5 h. Et_2NH (6.6 mL, 63 mmol) was added slowly to the reaction mixture at 0 °C and it was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure to give crude product, which was purified by column chromatography (hexane/EtOAc) to give **SM-17’** as a pale yellow solid (5.9 g, 98%). **SM-17** was prepared from **SM-17’** using Method C.

Viscous colorless oil (2.7 g, 41%). Rf 0.29 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.13-1.20 (br, 6H), 3.24-3.50 (br, 4H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.78 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.90 (dd, *J* = 7.0, 4.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.27-7.36 (m, 11H), 7.56 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 12.8, 14.1, 39.3, 43.3, 114.2, 117.6, 118.9, 124.2, 126.5, 128.3 (d, *J* = 7.6 Hz), 128.7, 129.0 (d, *J* = 16.3 Hz), 130.3, 131.7, 133.3, 134.0 (d, *J* = 21.1 Hz), 134.2, 135.7 (d, *J* = 10.6 Hz), 154.0, 157.6 (d, *J* = 16.3 Hz), 169.2. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 3055 w, 2975 w, 2935 w, 1623 m, 1461 m, 1432 s, 1286 m, 1256 m, 1239 s, 1196 m, 1097 m, 1066 w, 1044 w, 907 m, 728 s, 695 s. MS m/z (% relative intensity, CI): 534 (M^++3, 29), 533 (10), 532 (M^++1, 28), 455 (30), 454 (100), 453 (19), 452 (17), 376 (36). HRMS (CI): Calcd for $C_{29}H_{28}BrNO_2P$ 532.1041, Found 532.1039.

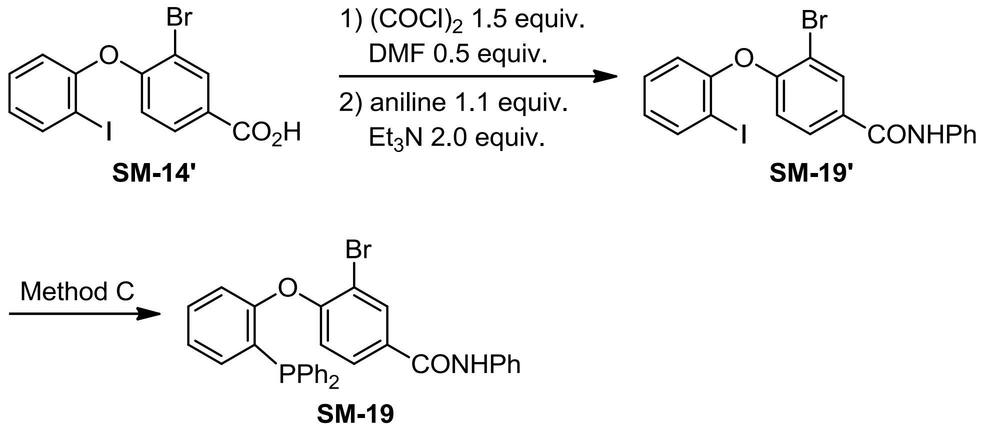
3-Bromo-4-(2-(diphenylphosphino)phenoxy)-*N*-methyl-*N*-phenylbenzamide (SM-18).



To a solution of PPh_3 (3.5 g, 13 mmol) and DDQ (3.0 g, 13 mmol) in CH_2Cl_2 (55 mL) was added *N*-methylaniline (1.4 mL, 13 mmol) and **SM-14’** (4.6 g, 11 mmol) successively at room temperature. After stirring overnight, the residue was washed with 1 M HCl aq. (30 mL) to remove the excess aniline and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography (hexane/EtOAc = 3/1) gave **SM-18'** as a pale yellow solid (2.7 g, 48%). **SM-18** was prepared from **SM-18'** using Method C.

White solid (0.56 g, 19%). Mp = 71 °C. Rf 0.34 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.46 (s, 3H), 6.44 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 7.2, 4.0 Hz, 1H), 6.86 (ddd, *J* = 7.6, 4.6, 1.6 Hz, 1H), 7.01 (t, *J* = 6.6 Hz, 4H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.21-7.32 (m, 13H), 7.54 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 38.5, 113.6, 117.4, 118.0, 124.2, 126.72, 126.74, 128.3 (d, *J* = 6.7 Hz), 128.7, 128.9 (d, *J* = 16.3 Hz), 129.1, 129.3, 130.2, 131.9, 133.9 (d, *J* = 20.1 Hz), 134.2, 134.4, 135.7 (d, *J* = 10.6 Hz), 144.5, 154.2, 157.6 (d, *J* = 16.3 Hz), 168.3. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.2. IR (ATR): 1640 m, 1493 w, 1462 m, 1434 m, 1362 m, 1240 m, 1196 w, 1106 w, 1066 w, 1044 w, 905 m, 730 s, 695 s, 671 m. MS m/z (% relative intensity, CI): 568 (M^{+}+3, 15), 566 (M^{+}+1, 14), 489 (22), 488 (63), 487 (12), 411 (29), 410 (100), 409 (12). HRMS (CI): Calcd for $C_{32}H_{26}BrNO_2P$ 566.0885, Found 566.0881.

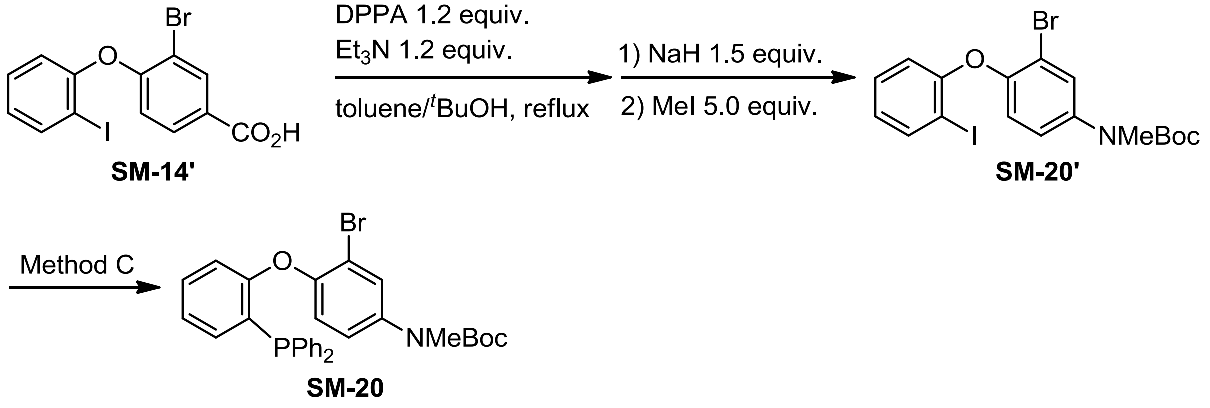
3-Bromo-4-(2-(diphenylphosphanyl)phenoxy)-*N*-phenylaniline (SM-19).



To a solution of **SM-14'** (4.2 g, 10 mmol) and DMF (0.40 mL, 5.0 mmol) in dry CH_2Cl_2 (95 mL) was added oxalyl chloride (1.3 mL, 15 mmol) dropwise at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for 5 h. Et_3N (2.8 mL, 20 mmol) and aniline (1.0 mL, 11 mmol) were added slowly to the reaction mixture at 0 °C and it was stirred at room temperature overnight. The reaction mixture was washed with sat. $NaHCO_3$ aq. (50 mL) and dried over $MgSO_4$. The solvent was then removed under reduced pressure to give crude product, which was purified by column chromatography (hexane/EtOAc = 5/1) to give **SM-19'** as a pale yellow solid (3.9 g, 79%). **SM-19** was prepared from **SM-19'** using Method C.

White solid (0.93 g, 21%). Mp = 90 °C. Rf 0.51 (hexane/EtOAc = 2/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.63 (d, *J* = 8.8 Hz, 1H), 6.87 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.94 (ddd, *J* = 7.7, 4.5, 1.7 Hz, 1H), 7.10-7.15 (m, 2H), 7.31-7.36 (m, 13H), 7.56-7.61 (m, 3H), 7.88 (brs, 1H), 8.02 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 113.7, 117.7, 118.9, 120.3, 124.7, 125.0, 127.4, 128.4 (d, *J* = 6.7 Hz), 128.8, 129.0, 130.0 (d, *J* = 16.4 Hz), 130.4, 130.5, 132.5, 134.0 (d, *J* = 20.1 Hz), 134.4, 135.5 (d, *J* = 9.6 Hz), 137.6, 156.5, 157.0 (d, *J* = 17.3 Hz), 163.8. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.1. IR (ATR): 3298 w, 1648 m, 1598 m, 1535 m, 1483 m, 1463 m, 1436 s, 1323 m, 1249 s, 1195 m, 1066 w, 1043 w, 906 m, 730 s, 692 s. HRMS (CI): Calcd for $C_{31}H_{24}BrNO_2P$ 552.0728, Found 552.0726.

***tert*-Butyl (3-bromo-4-(2-(diphenylphosphino)phenoxy)phenyl)(methyl)carbamate (SM-20).**

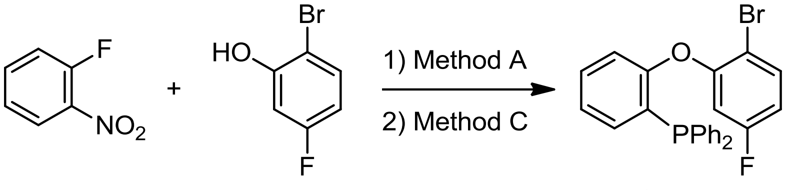


A solution of **SM-14’** (4.6 g, 11 mmol) in *t*-BuOH (63 mL) and toluene (63 mL) was treated with Et_3N (1.8 mL, 13 mmol), 3 Å molecular sieves (13 g) and diphenyl phosphoryl azide (2.7 mL, 13 mmol). The reaction mixture was warmed at reflux for 24 h and then cooled to room temperture. The solid was filtered off by passing the solution through Celite and the solvent was removed in vacuo. The residue was dissolved in EtOAc (75 mL), and the organic phase was washed with 1 M HCl aq. (50 mL×2), sat. $NaHCO_3$ aq. (50 mL×2), dried over $MgSO_4$, and concentrated. Silica gel chromatography (hexane/EtOAc = 5/1) afforded *tert*-butyl (3-bromo-4-(2-iodophenoxy)phenyl)carbamate as a pale yellow solid (4.2 g, 78%). *tert*-Butyl (3-bromo-4-(2-iodophenoxy)phenyl)carbamate (4.2 g, 8.6 mmol) was added slowly at 0 °C to a suspension of NaH (60% in mineral oil, 0.52 g, 13 mmol) in DMF (85 mL). After stirring at room temperature for 1 h, methyl iodide (2.7 mL, 43 mmol) was added. The reaction mixture was stirred at room temperature overnight, quenched with water, and extracted with CH_2Cl_2 (30 mL×2). The organic phase was dried over $MgSO_4$ and then evaporated. The residue was purified by chromatography to give **SM-20’** as a pale yellow solid (4.0 g, 91%). **SM-20** was prepared from **SM-20’** using Method C.

White solid (1.6 g, 37%). Mp = 65 °C. Rf 0.17 (hexane/EtOAc = 10/1). ^1H NMR ($CDCl_3$, 399.78 MHz) δ: 1.45 (s, 9H), 3.20 (s, 3H), 6.67-6.71 (m, 2H), 6.86 (ddd, *J* = 7.6, 4.6, 1.6 Hz, 1H), 6.99-7.04 (m, 2H), 7.23-7.28 (m, 1H), 7.31-7.39 (m, 10H), 7.42 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 28.3, 37.3, 80.7, 114.4, 116.3, 120.0, 123.5, 125.5, 128.1 (d, *J* = 15.4 Hz), 128.3 (d, *J* = 6.7 Hz), 128.7, 130.2, 130.4, 134.06 (d, *J* = 20.1 Hz), 134.09, 136.0 (d, *J* = 9.6 Hz), 140.3, 150.3, 154.4, 158.5 (d, *J* = 16.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.2. IR (ATR): 1699 s, 1488 s, 1463 m, 1434 s, 1364 m, 1254 s, 1232 s, 1150 s, 1111 m, 1066 w, 1041 w, 910 w, 863 w, 742 s, 697 s. MS m/z (% relative intensity, CI): 565 (11), 564 (M^++3, 32), 563 (13), 562 (M^++1, 33), 508 (16), 506 (21), 482 (18), 465 (27), 464 (100), 463

(38), 462 (99), 461 (11), 406 (12), 384 (22), 383 (19), 382 (45), 350 (21), 306 (19), 305 (13). HRMS (CI): Calcd for $C_{30}H_{30}BrNO_3P$ 562.1147, Found 562.1149.

(2-(2-Bromo-5-fluorophenoxy)phenyl)diphenylphosphine (SM-21).

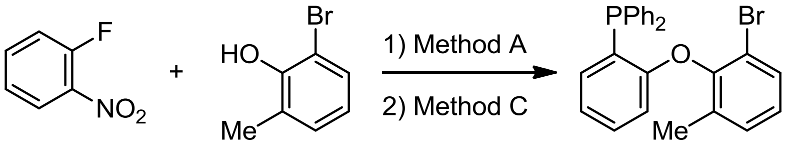


SM-21

This compound was synthesized from 1-fluoro-2-nitrobenzene and 2-bromo-5-fluorophenol (purchased from TCI) using Method A and Method C.

White solid (0.99 g, 26%). Mp = 92 °C. Rf 0.34 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.34 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.62 (td, *J* = 8.4, 2.8 Hz, 1H), 6.82 (dd, *J* = 7.4, 4.6 Hz, 1H), 6.92 (ddd, *J* = 7.6, 4.4, 1.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.29-7.37 (m, 11H), 7.44 (dd, *J* = 9.4, 5.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 106.6 (d, *J* = 26.7 Hz), 108.3 (d, *J* = 3.8 Hz), 111.3 (d, *J* = 23.0 Hz), 118.3, 124.7, 128.4 (d, *J* = 6.7 Hz), 128.8, 129.7 (d, *J* = 16.3 Hz), 130.4, 133.8 (d, *J* = 9.6 Hz), 134.1 (d, *J* = 21.1 Hz), 134.3 (d, *J* = 1.9 Hz), 135.7 (d, *J* = 9.7 Hz), 154.4 (d, *J* = 10.6 Hz), 157.2 (d, *J* = 16.3 Hz), 162.1 (d, *J* = 247.2 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 1596 m, 1582 m, 1476 m, 1462 m, 1433 m, 1408 w, 1258 m, 1203 m, 1146 m, 1117 m, 1066 w, 1040 w, 959 m, 855 m, 804 w, 778 w, 761 m, 743 s, 694 s. MS m/z (% relative intensity, CI): 454 (12), 453 (M^++3, 45), 452 (12), 451 (M^++1, 44), 389 (14), 374 (19), 373 (77), 372 (18), 371 (27), 351 (10), 296 (18), 295 (100), 294 (21), 217 (12). HRMS (CI): Calcd for $C_{24}H_{18}BrFOP$ 451.0263, Found 451.0255.

(2-(2-Bromo-6-methylphenoxy)phenyl)diphenylphosphine (SM-22).

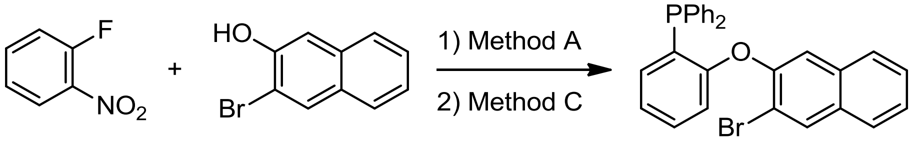


SM-22

This compound was synthesized from 1-fluoro-2-nitrobenzene and 2-bromo-6-methylphenol (purchased from TCI) using Method A and Method C.

White solid (2.9 g, 37%). Mp = 145 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.93 (s, 3H), 6.30 (dd, *J* = 7.2, 4.8 Hz, 1H), 6.80 (ddd, *J* = 7.3, 4.5, 1.9 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.33-7.35 (m, 6H), 7.39-7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 16.7, 111.6, 117.7, 122.0, 125.4 (d, *J* = 15.3 Hz), 126.3, 128.3, 128.35, 128.41, 128.6, 128.7, 130.0, 130.3, 131.2, 134.0 (d, *J* = 1.9 Hz), 134.2 (d, *J* = 20.1 Hz), 134.3 (d, *J* = 20.1 Hz), 136.1 (d, *J* = 11.5 Hz), 136.4 (d, *J* = 10.6 Hz), 149.6, 158.3 (d, *J* = 15.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.6. IR (ATR): 1569 w, 1458 m, 1431 m, 1258 w, 1221 m, 1178 w, 1134 w, 1092 w, 1067 w, 1026 w, 997 w, 875 w, 842 w, 797 w, 769 w, 745 s, 694 s. MS m/z (% relative intensity, CI): 450 (20), 449 (M^++3, 75), 448 (20), 447 (M^++1, 75), 370 (27), 369 (100), 368 (34), 367 (56), 291 (36), 290 (15), 185 (10). HRMS (CI): Calcd for $C_{25}H_{21}BrOP$ 447.0513, Found 447.0515.

(2-((3-Bromonaphthalen-2-yl)oxy)phenyl)diphenylphosphine (SM-23).

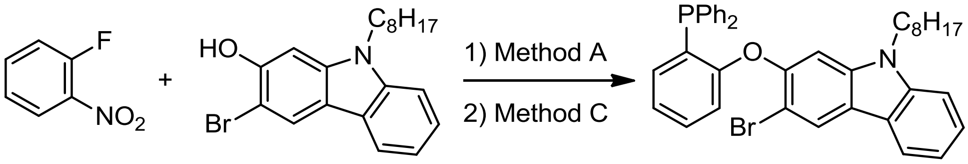


SM-23

This compound was synthesized from 1-fluoro-2-nitrobenzene and 3-bromo-2-naphthol (purchased from TCI) using Method A and Method C.

White solid (0.94 g, 36%). Mp = 82 °C. Rf 0.40 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.84 (dd, *J* = 8.0, 3.6 Hz, 1H), 6.94 (ddd, *J* = 7.5, 4.3, 1.7 Hz, 1H), 7.02 (s, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 7.29-7.33 (m, 7H), 7.36-7.42 (m, 6H), 7.51-7.53 (m, 1H), 7.67-7.69 (m, 1H), 8.05 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 114.6, 115.4, 117.8, 124.1, 125.5, 126.5, 126.6, 126.9, 128.3 (d, *J* = 7.6 Hz), 128.7, 129.1 (d, *J* = 15.3 Hz), 130.3, 130.9, 132.5, 133.0, 134.1 (d, *J* = 20.2 Hz), 134.3, 136.0 (d, *J* = 10.6 Hz), 151.0, 158.4 (d, *J* = 17.3 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.1. IR (ATR): 1569 w, 1434 m, 1353 w, 1324 w, 1239 m, 1216 m, 1166 w, 1092 w, 1066 w, 1026 w, 999 w, 908 m, 885 w, 799 w, 737 s, 694 s. MS m/z (% relative intensity, CI): 486 (24), 485 (M^++3, 81), 484 (24), 483 (M^++1, 81), 406 (10), 405 (36), 404 (29), 403 (67), 369 (10), 328 (23), 327 (100), 326 (28), 249 (14). HRMS (CI): Calcd for $C_{28}H_{21}BrOP$ 483.0513, Found 483.0516.

3-Bromo-2-(2-(diphenylphosphino)phenoxy)-9-octyl-9*H*-carbazole (SM-24).



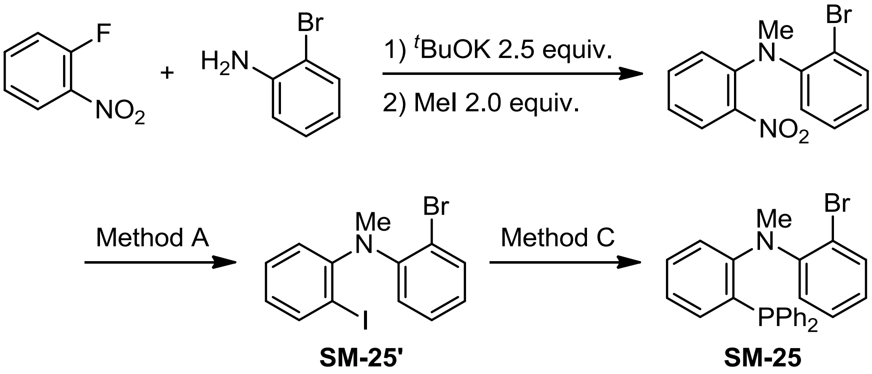
SM-24

This compound was synthesized from 1-fluoro-2-nitrobenzene and 3-bromo-2-hydroxy-9-octylcarbazole (prepared from 3-bromo-2-hydroxycarbazole according to a reported procedure[11]) using Method A and Method C.

White solid (0.94 g, 20%). Mp = 61 °C. Rf 0.40 (hexane/EtOAc = 1/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.85 (t, *J* = 7.2 Hz, 3H), 1.21-1.25 (m, 10H), 1.71 (quint, *J* = 7.3 Hz, 2H), 4.04 (t, *J* = 7.2 Hz, 2H), 6.62 (dd, *J* = 8.2, 4.6 Hz, 1H), 6.74 (s, 1H), 6.91 (t, *J* = 6.1 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.18-7.25 (m, 2H), 7.31-7.35 (m, 7H), 7.40-7.45 (m, 5H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.20 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 14.1, 22.6, 27.2, 28.8, 29.1, 29.3, 31.7, 13.1, 101.9, 106.1, 108.8, 115.2, 119.3, 120.1, 120.9, 121.5, 122.8, 124.4, 125.8, 127.1

(d, J = 15.3 Hz), 128.3 (d, J = 7.6 Hz), 128.7, 130.2, 134.1, 134.3, 136.3 (d, J = 10.6 Hz), 140.2, 140.9, 150.4, 159.7 (d, J = 15.3 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -16.0. IR (ATR): 3055 w, 2925 w, 2853 w, 1598 w, 1571 w, 1467 m, 1448 m, 1432 s, 1352 w, 1311 m, 1242 m, 1208 s, 1165 w, 1120 w, 1066 w, 1028 w, 908 m, 875 w, 849 w, 741 s, 696 s. MS m/z (% relative intensity, CI): 636 (M^++3, 20), 634(M^++1, 18), 557 (37), 556 (100), 555 (50), 554 (34), 479 (26), 478 (79), 477 (30). HRMS (CI): Calcd for $C_{38}H_{38}BrNOP$ 634.1874, Found 634.1872.

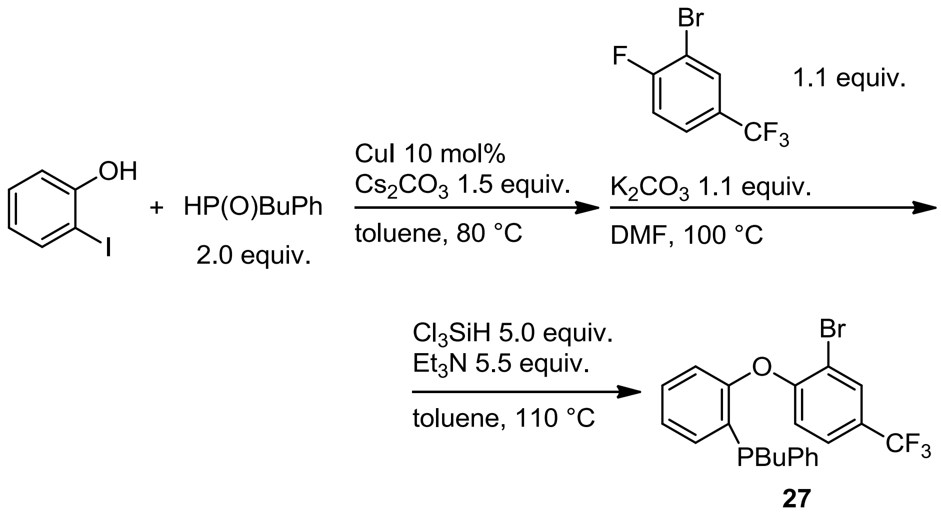
2-Bromo-*N*-(2-(diphenylphosphino)phenyl)-*N*-methylaniline (SM-25).



To a mixture of potassium *tert*-butoxide (11 g, 100 mmol) and 2-bromoaniline (6.9 g, 40 mmol) in DMSO (60 mL) was added dropwise 1-fluoro-2-nitrobenzene (5.6 g, 20 mmol) at 0 °C under an atmosphere of nitrogen. The resulting mixture was stirred at room temperature for 3 h, and then iodomethane (5.0 mL, 80 mmol) was added slowly. After 3 h, the reaction was quenched with water (80 mL) and extracted with EtOAc (80 mL×3). The combined organic extracts were washed with water (100 mL×3) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give crude 2-bromo-*N*-methyl-*N*-(2-nitrophenyl)aniline, which was directly used for the conversion to **SM-25’** according to Method A. **SM-25** was prepared from **SM-25’** using Method C.

White solid (0.67 g, 17%). Mp = 116 °C. Rf 0.46 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.17 (s, 3H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.99-7.04 (m, 3H), 7.10 (dd, *J* = 8.2, 5.0 Hz, 1H), 7.17 (t, *J* = 6.5 Hz, 4H), 7.24-7.26 (m, 6H), 7.30-7.35 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 43.2 (d, *J* = 4.7 Hz), 120.0, 122.9 (d, *J* = 3.8 Hz), 124.2 (d, *J* = 11.5 Hz), 124.7, 127.7, 128.07, 128.13, 130.0, 133.0 (d, *J* = 15.4 Hz), 133.5, 133.7, 134.2, 136.8, 137.7 (d, *J* = 12.5 Hz), 149.4, 155.0 (d, *J* = 23.0 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.5. IR (ATR): 3054 w, 3000 w, 2954 w, 2812 w, 1576 w, 1462 m, 1434 m, 1319 m, 1270 w, 1227 w, 1138 w, 1115 w, 1091 w, 1027 m, 872 m, 853 m, 743 s, 693 s. MS m/z (% relative intensity, CI): 449 (20), 448 (M^++3, 81), 447 (24), 446 (M^++1, 78), 368 (10), 367 (32), 366 (100), 290 (33), 289 (14). HRMS (CI): Calcd for $C_{25}H_{22}BrNP$ 446.0673, Found 446.0668.

(2-(2-Bromo-4-(trifluoromethyl)phenoxy)phenyl)(butyl)(phenyl)phosphine (27).



A mixture of 2-iodophenol (2.8 g, 13 mmol), butyl(phenyl)phosphine oxide[12] (2.3 g, 13 mmol), CuI (0.24 g, 1.3 mmol) and Cs_2CO_3 (6.3 g, 19 mmol) in touene (26 mL) was stirred at 80 °C for 12 h under an atmosphere of nitrogen. The reaction mixture was then filtered through a pad of Celite and the solvent was removed in vacuo. Purification by silica gel column chromatography (hexane/EtOAc = 2/1) afforded the crude butyl(2-hydroxyphenyl)(phenyl)phosphine oxide, which was used in the next step without further purification. A two-necked flask (100 mL) was charged with the crude butyl(2-hydroxyphenyl)(phenyl)phosphine oxide (0.92 mg, 3.4 mmol), 2-bromo-1-fluoro-4-(trifluoromethyl)benzene (0.90 g, 3.7 mmol, purchased from TCI,), K_2CO_3 (0.51 g, 3.7 mmol), and DMF (14 mL), and the mixture was heated at 100 °C for 12 h. The mixture was then allowed to cool to room temperature and filtered through a pad of Celite. The filtrate was poured into water and the resulting mixture was extracted with ethyl acetate (30 mL×3). After the combined extracts were dried over $MgSO_4$, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 5/1) to give (2-(2-bromo-4-(trifluoromethyl)phenoxy)phenyl) (butyl)(phenyl)phosphine oxide as a pale brown oil (0.90 g, 14% over two steps). A solution of the obtained phosphine oxide (0.90 g, 1.8 mmol) in toluene (23 mL) was frozen using an EtOH/liquid nitrogen bath, to which trichlorosilane (0.91 mL, 9.0 mmol) and triethylamine (1.4 mL, 9.9 mmol) were added. The mixture was stirred at 110 °C under nitrogen overnight. After cooling to room temperature, sat. $NaHCO_3$ aq. (2 mL) was added, and the mixture was stirred for 5 min. The mixture was filtered through a pad of alumina and evaporated in vacuo to give the crude product. Purification by flash chromatography (hexane/EtOAc = 10/1) gave **27** as colorless oil.

Colorless oil (0.59 g, 68%). Rf 0.49 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.88 (t, J = 6.8 Hz, 3H), 1.41-1.47 (m, 4H), 2.05-2.26 (m, 2H), 6.45 (d, J = 8.8 Hz, 1H), 6.84 (dd, J = 8.2, 3.4 Hz, 1H), 7.19-7.26 (m, 5H), 7.31-7.43 (m, 4H), 7.81 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 13.8, 24.4 (d, J = 13.4 Hz), 25.9 (d, J = 10.6 Hz), 28.1 (d, J = 16.3 Hz), 113.0, 116.9, 119.8, 123.3 (quart, J = 272.1 Hz), 125.3, 125.4, 125.6 (quart, J = 36.5 Hz), 128.3 (d, J = 7.6 Hz), 128.7, 130.1, 130.7 (quart, J = 3.8 Hz), 132.2 (d, J = 20.1 Hz), 133.1, 133.3, 136.9 (d, J = 12.5 Hz), 156.7 (d, J = 13.5 Hz), 156.8. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -25.7. IR (ATR): 3069 w, 2957 w, 2928 w, 2871 w, 1608 w, 1494 w, 1465 w, 1435 w, 1403 w, 1321 s, 1262 m, 1193 w, 1170 m, 1125 s, 1076 m, 1047 w, 890 w, 820 w, 781 w, 744 m, 696 w. MS m/z (% relative intensity, CI): 525 (11), 523 (13), 499 (10), 497 (10), 484 (24), 483 (M^++3, 97), 482 (25), 481 (M^++1, 100), 403 (10), 402 (21), 401 (78), 346 (13), 345 (60), 344 (18), 324 (14), 267 (16). HRMS (CI): Calcd for $C_{23}H_{22}BrF_3OP$ 481.0544, Found 481.0538.

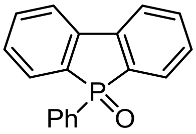
General Procedure for the synthesis of phosphole oxides (Table 2.1).

An oven-dried 5-mL screw-capped vial was charged with **4** (0.15 mg, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), Et_3SiH (57 μL, 0.36 mmol) and DMA (0.6 mL) under a gentle stream of nitrogen. The vessel was heated at 130 °C for 6 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by flash chromatography (EtOAc) to give **3** (59 mg, 71%) as a white solid.

General Procedure for the synthesis of phenoxaphosphinine oxides (Table 2.3).

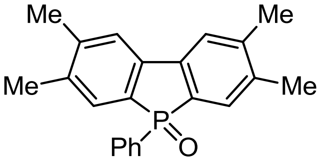
An oven-dried 5-mL screw-capped vial was charged with **SM-12** (0.13 g, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), $(Me_3Si)_3SiH$ (90 mg, 0.11 mL, 0.36 mmol), and DMF (0.6 mL) under a gentle stream of nitrogen. The vessel was heated at 130 °C for 12 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by flash chromatography (EtOAc) to give **12** (74 mg, 85%) as a white solid.

5-Phenyl-5*H*-benzophosphole 5-oxide (3) [CAS: 19190-40-0]



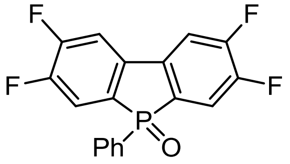
White solid. (74 mg, 89% from **1**; 59 mg, 71% from **4**). Rf 0.40 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.35-7.40 (m, 4H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.62-7.73 (m, 4H), 7.82 (dd, *J* = 7.8, 2.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 121.1 (d, *J* = 10.6 Hz), 128.7 (d, *J* = 12.5 Hz), 129.4 (d, *J* = 10.6 Hz), 129.8 (d, *J* = 9.6 Hz), 130.7 (d, *J* = 103.5 Hz), 131.0 (d, *J* = 10.6 Hz), 132.1 (d, *J* = 2.9 Hz), 132.8 (d, *J* = 107.4 Hz), 133.3 (d, *J* = 1.9 Hz), 141.7 (d, *J* = 21.0 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 34.0. HRMS (EI): Calcd for $C_{18}H_{13}OP$ 276.0704, found: 276.0701.

2,3,7,8-Tetramethyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (5).



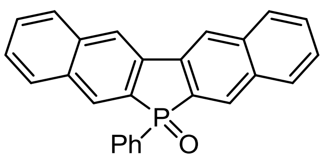
White solid. (95 mg, 95%). Mp = 264 °C. Rf 0.46 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.23 (s, 6H), 2.34 (s, 6H), 7.36 (td, *J* = 7.5, 2.9 Hz, 2H), 7.41-7.47 (m, 3H), 7.53 (d, *J* = 2.8 Hz, 2H), 7.65 (dd, *J* = 12.8, 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 19.7, 20.5, 121.9 (d, *J* = 11.6 Hz), 128.5 (d, *J* = 12.5 Hz), 130.1 (d, *J* = 108.3 Hz), 130.5 (d, *J* = 9.7 Hz), 130.9 (d, *J* = 10.6 Hz), 131.69 (d, *J* = 103.4 Hz), 131.70 (d, *J* = 1.9 Hz), 137.6 (d, *J* = 11.5 Hz), 140.0 (d, *J* = 22.0 Hz), 142.3 (d, *J* = 1.9 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 34.1. IR (ATR): 3021 w, 2971 w, 2941 w, 1739 m, 1607 w, 1476 w, 1436 m, 1370 m, 1198 s, 1157 m, 1111 m, 1018 w, 909 w, 887 w, 737 m, 693 m, 660 m. MS m/z (% relative intensity): 333 (26), 332 (M^+, 100), 285 (16), 284 (17), 270 (16), 255 (46), 239 (27). HRMS (EI): Calcd for $C_{22}H_{21}OP$ 332.1330, found: 332.1329.

2,3,7,8-Tetrafluoro-5-phenyl-5*H*-dibenzophosphole 5-oxide (6).



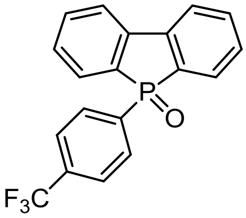
White solid. (66 mg, 63%). Mp = 221 °C. Rf 0.69 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.43-7.49 (m, 3H), 7.51-7.64 (m, 6H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 111.0 (dd, *J* = 9.6, 12.0 Hz), 119.2 (dd, *J* = 9.3, 12.0 Hz), 128.6 (d, *J* = 107.3 Hz), 129.1 (d, *J* = 13.4 Hz), 129.8 (d, *J* = 106.4 Hz), 130.9 (d, *J* = 11.5 Hz), 133.0 (d, *J* = 2.9 Hz), 137.3 (d, *J* = 21.1 Hz), 151.3 (ddd, *J* = 256.6, 17.0, 13.7 Hz), 154.3 (dd, *J* = 257.7, 13.4 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: 30.9. IR (ATR): 1601 m, 1491 s, 1439 w, 1410 s, 1353 m, 1283 s, 1267 s, 1205 s, 1165 m, 1111 s, 1017 s, 904 m, 879 m, 850 w, 776 m, 731 s, 688 s, 661 m. MS m/z (% relative intensity): 349 (21), 348 (M$^+$, 100), 347 (11), 302 (14), 301 (86), 300 (65), 281 (18), 280 (13), 271 (49), 255 (49), 224 (36). HRMS (EI): Calcd for C$_{18}$H$_9$F$_4$OP 348.0327, found: 348.0327.

6-Phenyl-6H-benzo[*f*]naphtho[2,3-*b*]phosphindole 6-oxide (7).



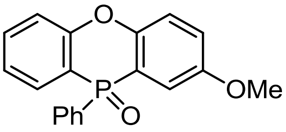
White solid. (74 mg, 66%). Mp = 325 °C. Rf 0.51 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.38 (td, *J* = 7.4, 2.7 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 3H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.70 (dd, *J* = 13.0, 7.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 8.28 (d, *J* = 11.2 Hz, 2H), 8.41 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 120.3 (d, *J* = 8.6 Hz), 127.0, 128.5, 128.61, 128.63 (d, *J* = 12.5 Hz), 129.2, 131.2 (d, *J* = 11.6 Hz), 131.4 (d, *J* = 107.3 Hz), 131.7 (d, *J* = 9.7 Hz), 132.028, (d, *J* = 2.9 Hz), 132.033 (d, *J* = 105.5 Hz), 133.6 (d, *J* = 12.5 Hz), 135.9, 137.4 (d, *J* = 21.1 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: 32.0. IR (ATR): 1627 w, 1598 w, 1496 w, 1434 w, 1327 w, 1273 w, 1223 w, 1189 s, 1136 w, 1113 m, 1079 w, 1020 w, 956 w, 900 m, 869 m, 744 s, 730 m, 692 m, 666 w. MS m/z (% relative intensity): 377 (28), 376 (M^+, 100), 329 (23), 328 (27), 300 (12), 299 (54), 283 (24), 252 (15). HRMS (EI): Calcd for $C_{26}H_{17}OP$ 376.1017, found: 376.1019.

3-Fluoro-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (8).



White solid. (72 mg, 70%). Rf 0.54 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.41 (td, *J* = 7.3, 3.7 Hz, 2H), 7.61-7.65 (m, 4H), 7.69-7.80 (m, 4H), 7.86 (dd, *J* = 7.6, 2.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 121.4 (d, *J* = 10.6 Hz), 123.5 (q, *J* = 273.0 Hz), 125.5-125.6 (m), 129.7 (d, *J* = 10.6 Hz), 129.9 (d, *J* = 9.6 Hz), 131.5 (d, *J* = 11.5 Hz), 131.9 (d, *J* = 108.3 Hz), 133.8, 133.9 (qd, *J* = 32.6, 2.9 Hz), 135.5 (d, *J* = 100.6 Hz), 141.8 (d, *J* = 22.1 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 32.5. HRMS (EI): Calcd for $C_{19}H_{12}F_3OP$ 344.0578, found: 344.0581.

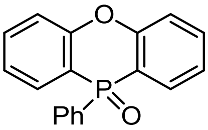
2-Methoxy-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (10).



White solid. (56 mg, 86%). Mp = 143 °C. Rf 0.40 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.76 (s, 3H), 7.12-7.17 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.27-7.34 (m, 2H), 7.39-7.48 (m, 3H), 7.57 (t, *J* = 7.9 Hz, 1H), 7.63 (dd, *J* = 13.3, 7.7 Hz, 2H), 7.75 (ddd, *J* = 13.0, 7.8, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.8, 111.7 (d, *J* = 6.6 Hz), 114.5 (d, *J* = 104.5 Hz), 115.1 (d, *J* = 102.4 Hz), 118.1 (d, *J* = 6.6 Hz), 119.8 (d, *J* = 7.6 Hz), 122.4, 123.8 (d, *J* = 10.6

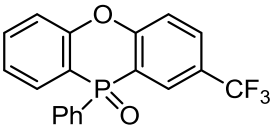
Hz), 128.5 (d, *J* = 12.5 Hz), 131.0 (d, *J* = 4.7 Hz), 131.3 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 2.9 Hz), 133.6, 134.0 (d, *J* = 115.9 Hz), 149.9 (d, *J* = 2.9 Hz), 155.6 (d, *J* = 4.7 Hz), 155.7 (d, *J* = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 0.64. IR (ATR): 1610 w, 1584 w, 1486 m, 1469 m, 1437 m, 1402 m, 1318 m, 1271 s, 1235 m, 1217 m, 1195 s, 1163 m, 1135 m, 1116 m, 1075 w, 1033 m, 908 w, 859 m, 845 m, 832 m, 755 s, 729 m, 715 m, 696 s. MS m/z (% relative intensity): 323 (18), 322 (M^+, 100), 321 (48), 307 (31), 245 (58), 229 (16), 202 (14). HRMS (EI): Calcd for $C_{19}H_{15}O_3P$ 322.0759, found: 322.0757.

10-Phenyl-10*H*-phenoxaphosphinine 10-oxide (12).



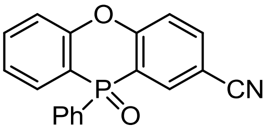
White solid. (74 mg, 85%). Mp = 175 °C. Rf 0.51 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.23 (t, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.38-7.48 (m, 3H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.64 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.74 (ddd, *J* = 13.3, 7.7, 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.2 (d, *J* = 102.5 Hz), 118.2 (d, *J* = 5.7 Hz), 124.0 (d, *J* = 10.6 Hz), 128.4 (d, *J* = 13.5 Hz), 131.1 (d, *J* = 4.8 Hz), 131.4 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 11.6 Hz), 133.7, 133.9 (d, *J* = 115.9 Hz), 155.5 (d, *J* = 11.6 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.36. IR (ATR): 1712 w, 1594 m, 1581 m, 1462 m, 1427 s, 1363 w, 1321 m, 1269 s, 1217 m, 1195 s, 1157 m, 1130 m, 1116 m, 1083 m, 1067 w, 882 m, 752 s, 728 s, 705 s, 690 s. MS m/z (% relative intensity): 293 (19), 292 (M^+, 100), 291 (94), 216 (12), 215 (84), 199 (43), 168 (28), 139 (24), 51 (10). HRMS (EI): Calcd for $C_{18}H_{13}O_2P$ 292.0653, found: 292.0652.

10-Phenyl-2-(trifluoromethyl)-10*H*-phenoxaphosphinine 10-oxide (13).



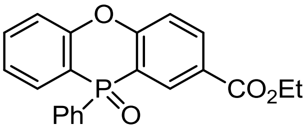
White solid. (89 mg, 83%). Mp = 121 °C. Rf 0.57 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.30 (t, *J* = 7.4 Hz, 1H), 7.39-7.53 (m, 5H), 7.61-7.66 (m, 3H), 7.73-7.83 (m, 2H), 8.03 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.0 (d, *J* = 104.5 Hz), 116.0 (d, *J* = 100.5 Hz), 118.4 (d, *J* = 5.8 Hz), 119.2 (d, *J* = 5.7 Hz), 123.3 (quart, *J* = 272.1 Hz), 124.8 (d, *J* = 10.6 Hz), 126.4 (quart d, *J* = 33.5, 10.5 Hz), 128.7 (d, *J* = 12.4 Hz), 128.9-129.1 (m), 130.5, 131.2 (d, *J* = 5.7 Hz), 131.4 (d, *J* = 11.5 Hz), 132.2 (d, *J* = 2.8 Hz), 133.0 (d, *J* = 116.9 Hz), 134.2, 155.1 (d, *J* = 2.9 Hz), 157.4. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.90. IR (ATR): 1621 w, 1604 w, 1587 w, 1474 w, 1442 m, 1407 w, 1329 m, 1315 m, 1270 s, 1230 w, 1200 s, 1174 m, 1119 s, 1088 s, 1070 s, 898 m, 831 m, 771 m, 752 m, 732 m, 696 m, 658 w. MS m/z (% relative intensity): 361 (19), 360 (M^+, 100), 359 (87), 296 (12), 284 (11), 283 (74), 267 (61), 217 (21), 199 (14), 139 (11), 51 (12). HRMS (EI): Calcd for $C_{19}H_{12}F_3O_2P$ 360.0527, found: 360.0526.

2-Cyano-10-Phenyl-10*H*-phenoxaphosphinine 10-oxide (14).



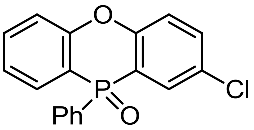
White solid. (70 mg, 73%). Mp = 212 °C. Rf 0.57 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.33 (t, *J* = 7.2 Hz, 1H), 7.40-7.51 (m, 4H), 7.53-7.57 (m, 1H), 7.60-7.69 (m, 3H), 7.75 (ddd, *J* = 13.3, 7.7, 1.7 Hz, 1H), 7.82 (dd, *J* = 9.0, 2.2 Hz, 1H), 8.05 (dd, *J* = 12.8, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 108.1 (d, *J* = 12.5 Hz), 114.8 (d, *J* = 104.5 Hz), 117.36, 117.37 (d, *J* = 99.6 Hz), 118.5 (d, *J* = 6.6 Hz), 119.7 (d, *J* = 5.7 Hz), 125.2 (d, *J* = 10.6 Hz), 128.8 (d, *J* = 12.5 Hz), 131.3 (d, *J* = 5.7 Hz), 131.5 (d, *J* = 10.5 Hz), 132.4 (d, *J* = 117.9 Hz), 132.5 (d, *J* = 2.8 Hz), 134.4, 136.3, 136.6 (d, *J* = 5.7 Hz), 155.0 (d, *J* = 3.8 Hz), 157.6 (d, *J* = 2.9 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -1.7. IR (ATR): 2231 m, 1599 m, 1578 w, 167 m, 1436 s, 1394 s, 1325 m, 1282 s, 1271 s, 1198 s, 1165 m, 1149 w, 1134 m, 1114 s, 1085 m, 925 w, 903 m, 823 m, 751 s, 728 s, 699 s. MS m/z (% relative intensity): 318 (17), 317 (M^+, 88), 316 (100), 240 (52), 224 (42), 193 (18), 51 (13). HRMS (EI): Calcd for $C_{19}H_{12}NO_2P$ 317.0606, found: 317.0603.

Ethyl 10-phenyl-10*H*-phenoxaphosphinine-2-carboxylate 10-oxide (15).



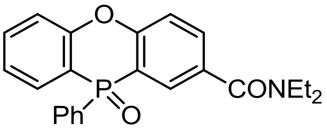
White solid. (85 mg, 77%). Mp = 131 °C. Rf 0.49 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.35 (t, *J* = 7.2 Hz, 3H), 4.26-4.41 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.37-7.51 (m, 5H), 7.60-7.66 (m, 3H), 7.76 (ddd, *J* = 13.0, 7.8, 1.6 Hz, 1H), 8.25 (dd, *J* = 8.8, 2.0 Hz, 1H), 8.48 (dd, *J* = 13.4, 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 14.2, 61.3, 115.2 (d, *J* = 103.4 Hz), 115.3 (d, *J* = 101.5 Hz), 118.3 (d, *J* = 6.7 Hz), 118.5 (d, *J* = 5.8 Hz), 124.7 (d, *J* = 10.6 Hz), 126.4 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 12.5 Hz), 131.2 (d, *J* = 4.8 Hz), 131.4 (d, *J* = 10.6 Hz), 132.0 (d, *J* = 2.8 Hz), 133.5 (d, *J* = 118.8 Hz), 133.7 (d, *J* = 5.7 Hz), 134.0, 134.7, 155.1 (d, *J* = 2.8 Hz), 158.2 (d, *J* = 3.8 Hz), 164.8. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.74. IR (ATR): 1712 s, 1599 m, 1464 m, 1436 m, 1393 m, 1368 w, 1331 m, 1279 m, 1252 s, 1195 s, 1173 m, 1136 m, 1107 s, 1085 m, 1024 m, 910 w, 877 w, 847 w, 763 s, 727 s, 694 m, 661 w. MS m/z (% relative intensity): 365 (22), 364 (M^+, 100), 363 (42), 336 (23), 335 (91), 320 (10), 319 (42), 292 (51), 291 (11), 287 (41), 271 (45), 259 (55), 243 (19), 215 (14), 199 (11), 139 (25). HRMS (EI): Calcd for $C_{21}H_{17}O_4P$ 364.0864, found: 364.0866.

2-Chloro-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (16).



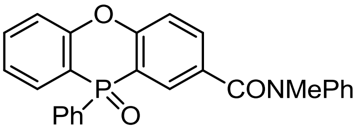
White solid. (70 mg, 71%). Mp = 148 °C. Rf 0.54 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.24-7.38 (m, 3H), 7.42-7.46 (m, 2H), 7.49-7.53 (m, 2H), 7.59-7.76 (m, 5H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 114.6 (d, *J* = 104.5 Hz), 117.0 (d, *J* = 99.6 Hz), 118.3 (d, *J* = 5.7 Hz), 120.1 (d, *J* = 6.7 Hz), 124.4 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 13.5 Hz), 129.3 (d, *J* = 13.4 Hz), 130.3 (d, *J* = 5.8 Hz), 131.2 (d, *J* = 5.7 Hz), 131.5 (d, *J* = 11.5 Hz), 132.1 (d, *J* = 2.8 Hz), 133.2 (d, *J* = 116.9 Hz), 133.95, 134.04, 153.9 (d, *J* = 2.9 Hz), 155.4 (d, *J* = 2.8 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.58. IR (ATR): 1591 w, 1460 s, 1435 s, 1389 m, 1323 m, 1268 s, 1200 s, 1164 m, 1137 m, 1103 m, 891 w, 877 w, 829 m, 760 s, 726 s, 695 s, 665 m. MS m/z (% relative intensity): 328 (32), 327 (47), 326 (M^+, 100), 325 (89), 251 (21), 249 (66), 235 (13), 233 (41), 202 (16), 199 (14), 186 (14), 139 (29), 51 (11). HRMS (EI): Calcd for $C_{18}H_{12}ClO_2P$ 326.0263, found: 326.0260.

_N, N_-Diethyl-10-phenyl-10_H_-phenoxaphosphinine-2-carboxamide 10-oxide (17).



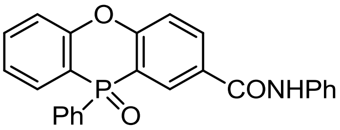
Viscous colorless oil. (85 mg, 72%). Rf 0.23 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.04-1.21 (br, 6H), 3.21-3.55 (br, 4H), 7.25-7.29 (m, 1H), 7.36-7.49 (m, 5H), 7.58-7.65 (m, 4H), 7.71-7.77 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 12.7, 14.1, 39.5, 43.5, 115.1 (d, *J* = 103.4 Hz), 115.3 (d, *J* = 101.5 Hz), 118.3 (d, *J* = 6.6 Hz), 118.7 (d, *J* = 6.7 Hz), 124.4 (d, *J* = 10.5 Hz), 128.6 (d, *J* = 12.5 Hz), 129.3 (d, *J* = 5.8 Hz), 131.2 (d, *J* = 4.8 Hz), 131.5 (d, *J* = 10.6 Hz), 132.0 (d, *J* = 1.9 Hz), 132.3, 132.9 (d, *J* = 9.6 Hz), 133.3 (d, *J* = 115.9 Hz), 134.0, 155.4 (d, *J* = 2.9 Hz), 155.8 (d, *J* = 2.9 Hz), 169.4. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.44. IR (ATR): 1627 m, 1599 m, 1465 m, 1436 s, 1388 m, 1320 m, 1267 s, 1198 s, 1164 m, 1134 m, 1116 m, 1088 m, 907 w, 841 w, 822 w, 750 s, 728 m, 694 m, 664 w. MS m/z (% relative intensity): 391 (M^+, 19), 390 (50), 320 (31), 319 (100), 292 (38), 291 (10), 263 (12), 215 (10), 72 (13). HRMS (EI): Calcd for $C_{23}H_{22}NO_3P$ 391.1337, found: 391.1336.

_N_-Methyl-_N_-phenyl-10-phenyl-10_H_-phenoxaphosphinine-2-carboxamide 10-oxide (18).



White solid. (97 mg, 76%). Mp = 184 °C. Rf 0.31 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.44 (s, 3H), 6.94-6.97 (m, 3H), 7.07 (t, *J* = 7.8 Hz, 2H), 7.17-7.24 (m, 2H), 7.30 (dd, *J* = 8.4, 5.6 Hz, 1H), 7.35-7.50 (m, 5H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.61-7.69 (m, 3H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 38.4, 114.5 (d, *J* = 101.5 Hz), 115.2 (d, *J* = 103.4 Hz), 117.9 (d, *J* = 5.8 Hz), 118.2 (d, *J* = 5.7 Hz), 124.4 (d, *J* = 10.6 Hz), 126.6, 126.7, 128.5 (d, *J* = 13.5 Hz), 129.1, 131.1 (d, *J* = 5.7 Hz), 131.4 (d, *J* = 10.6 Hz), 131.5 (d, *J* = 10.5 Hz), 131.7 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 6.7 Hz), 133.3 (d, *J* = 116.0 Hz), 133.9, 134.3, 144.3, 155.1 (d, *J* = 2.9 Hz), 155.9 (d, *J* = 2.9 Hz), 168.5. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.98. IR (ATR): 1631 s, 1595 m, 1496 w, 1468 m, 1435 m, 1387 m, 1370 s, 1322 m, 1270 s, 1228 m, 1209 m,1197 m, 1162 w, 1137 m, 1107 m, 1083 m, 1029 w, 998 w, 907 m, 877 w, 831 w, 819 w, 781 w, 748 s, 725 m, 696 s, 657 w. MS m/z (% relative intensity): 425 (M^+, 32), 320 (21), 319 (100). HRMS (EI): Calcd for $C_{26}H_{20}NO_3P$ 425.1181, found: 425.1183.

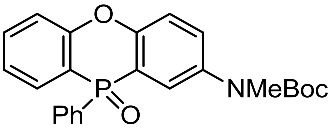
_N_,10-Diphenylphenoxaphosphinine-2-carboxamide 10-oxide (19).



White solid. (42 mg, 68%). Mp = 304 °C. Rf 0.49 (EtOAc). ^{1}H NMR (DMSO-d_6, 399.78 MHz) δ: 7.11 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.51-7.59 (m, 6H), 7.65-7.80 (m, 5H), 8.32-8.38 (m, 2H), 10.4 (s, 1H). ^{13}C NMR (DMSO-d_6, 100.53

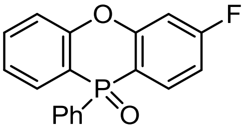
MHz) δ: 115.8 (d, *J* = 100.6 Hz), 115.9 (d, *J* = 101.5 Hz), 119.0 (d, *J* = 5.8 Hz), 119.2 (d, *J* = 5.7 Hz), 121.1, 124.4, 125.5 (d, *J* = 10.6 Hz), 129.0, 129.4 (d, *J* = 12.5 Hz), 131.1 (d, *J* = 9.7 Hz), 131.3 (d, *J* = 6.6 Hz), 131.4 (d, *J* = 10.6 Hz), 131.9, 132.6, 134.2, 134.5 (d, *J* = 114.0 Hz), 135.1, 139.3, 155.0 (d, *J* = 2.8 Hz), 157.3 (d, *J* = 2.8 Hz), 163.9. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 0.80. IR (ATR): 3324w, 1666 m, 1603 m, 1544 m, 1498 w, 1469 w, 1437 m, 1398 w, 1330 m, 1291 w, 1274 w, 1245 s, 1181 s, 1162 m, 1130 m, 1086 w, 922 m, 853 w, 753 s, 729 m, 691 s. MS m/z (% relative intensity): 412 (M^++1, 11), 411 (M^+, 36), 320 (21), 319 (100). HRMS (EI): Calcd for $C_{25}H_{18}NO_3P$ 411.1024, found: 411.1027.

***tert*-Butyl methyl(10-oxido-10-phenyl-10*H*-phenoxaphosphinin-2-yl)carbamate (20).**



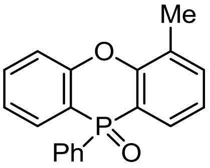
White solid. (98 mg, 77%). Mp = 58 °C. Rf 0.40 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 1.32 (s, 9H), 3.21 (s, 3H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.30-7.36 (m, 2H), 7.39-7.54 (m, 5H), 7.56-7.66 (m, 3H), 7.73 (dd, *J* = 13.0, 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 28.1, 37.1, 80.6, 114.8 (d, *J* = 102.4 Hz), 115.1 (d, *J* = 101.5 Hz), 118.2 (d, *J* = 6.7 Hz), 118.6 (d, *J* = 6.7 Hz), 124.1 (d, *J* = 10.6 Hz), 128.5 (d, *J* = 13.4 Hz), 131.1 (d, *J* = 4.8 Hz), 131.4 (d, *J* = 11.6 Hz), 131.6, 131.8 (d, *J* = 2.9 Hz), 133.76 (d, *J* = 116.9 Hz), 133.79, 139.8 (d, *J* = 12.5 Hz), 152.7 (d, *J* = 2.9 Hz), 154.2, 154.5 (d, *J* = 3.8 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -0.17. IR (ATR): 2976 w, 1695 s, 1601 w, 1583 w, 1485 m, 1467 m, 1437 s, 1406 m, 1364 m, 1315 m, 1289 m, 1268 s, 1199 s, 1148 s, 1113 s, 1086 m, 1029 w, 988 w, 896 m, 860 m, 829 w, 756 s, 729 s, 694 s, 660 w. MS m/z (% relative intensity, CI): 422 (M^++1, 30), 366 (24), 323 (20), 322 (100), 321 (22). HRMS (CI): Calcd for $C_{24}H_{25}NO_4P$ 422.1521, found: 422.1520.

3-Fluoro-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (21).



White solid. (69 mg, 74%). Mp = 185 °C. Rf 0.66 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 6.97-7.01 (m, 1H), 7.07 (ddd, *J* = 9.8, 4.8, 2.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.40-7.51 (m, 3H), 7.58-7.66 (m, 3H), 7.70-7.77 (m, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 105.4 (dd, *J* = 24.4, 7.2 Hz), 111.7 (dd, *J* = 105.4, 2.9 Hz), 112.7 (dd, *J* = 22.0, 11.6 Hz), 115.2 (d, *J* = 103.5 Hz), 118.2 (d, *J* = 5.7 Hz), 124.5 (d, *J* = 11.5 Hz), 128.5 (d, *J* = 13.4 Hz), 131.2 (d, *J* = 4.8 Hz), 131.5 (d, *J* = 10.6 Hz), 131.9 (d, *J* = 2.9 Hz), 133.5 (dd, *J* = 10.5, 5.8 Hz), 133.6 (d, *J* = 116.9 Hz), 133.9, 155.4 (d, *J* = 2.8 Hz), 157.0 (dd, *J* = 12.9, 4.3 Hz), 165.6 (dd, *J* = 253.9, 1.9 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: -0.60. IR (ATR): 1599 m, 1585 m, 1469 m, 1440 m, 1407 s, 1330 m, 1275 m, 1221 m, 1196 s, 1164 m, 1130 m, 1113 m, 1084 m, 975 m, 951 w, 852 m, 814 m, 752 s, 726 s, 697 s, 670 w. MS m/z (% relative intensity): 310 (M$^+$, 87), 309 (91), 233 (100), 217 (30). HRMS (EI): Calcd for $C_{18}H_{12}FO_2P$ 310.0559, found: 310.0556.

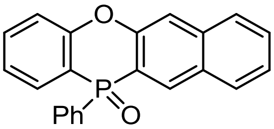
4-Methyl-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (22).



White solid. (79 mg, 86%). Mp = 130 °C. Rf 0.54 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 2.51 (s, 3H), 7.12 (td, *J* = 7.4, 1.6 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.37-7.47 (m, 5H), 7.54-7.66 (m, 4H), 7.73 (ddd, *J* = 12.9, 7.7, 1.5 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 16.6, 114.7 (d, *J* = 102.5 Hz), 115.2 (d, *J* = 102.5 Hz), 118.3 (d, *J* = 5.8 Hz), 123.5 (d, *J* = 11.5 Hz), 124.0 (d, *J* = 10.6 Hz), 127.0 (d, *J* = 6.7 Hz), 128.4 (d, *J* = 13.5 Hz), 128.7 (d, *J* = 4.8 Hz), 131.1 (d, *J* = 5.7 Hz), 131.4 (d, *J* = 11.5 Hz), 131.6 (d, *J* = 1.9 Hz), 133.6, 134.0 (d, *J*

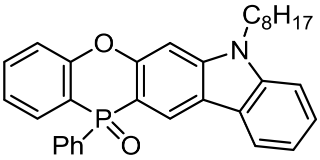
= 115.9 Hz), 134.8, 153.7 (d, *J* = 2.9 Hz), 155.6 (d, *J* = 2.9 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 0.29. IR (ATR): 1592 w, 1458 m, 1436 m, 1415 s, 1331 w, 1271 m, 1227 m, 1201 s, 1183 m, 1159 m, 1133 m, 1112 m, 1083 w, 882 m, 778 m, 755 s, 730 s, 701 s, 665 w. MS m/z (% relative intensity): 307 (19), 306(M^+, 100), 305 (89), 230 (11), 229 (84), 213 (30), 199 (10), 182 (10), 181 (22), 152 (15). HRMS (EI): Calcd for $C_{19}H_{15}O_2P$ 306.0810, found: 306.0809.

12-Phenyl-12*H*-benzo[*b*]phenoxaphosphinine 12-oxide (23).



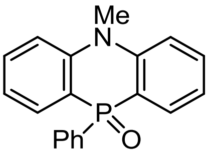
White solid. (90 mg, 87%). Mp = 156 °C. Rf 0.60 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.25 (t, *J* = 7.4 Hz, 1H), 7.37-7.46 (m, 5H), 7.53-7.62 (m, 2H), 7.64-7.69 (m, 2H), 7.78 (d, *J* = 5.2 Hz, 1H), 7.81-7.85 (m, 3H), 8.43 (d, *J* = 14.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 113.8 (d, *J* = 5.7 Hz), 115.4 (d, *J* = 103.5 Hz), 117.1 (d, *J* = 101.6 Hz), 118.3 (d, *J* = 6.6 Hz), 123.9 (d, *J* = 10.6 Hz), 125.5, 127.0, 128.5 (d, *J* = 2.9 Hz), 128.7 (d, *J* = 13.4 Hz), 129.7 (d, *J* = 11.6 Hz), 131.0, 131.05, 131.11, 131.7 (d, *J* = 2.0 Hz), 133.5 (d, *J* = 4.8 Hz), 134.0, 134.3 (d, *J* = 115.0 Hz), 135.9, 151.8 (d, *J* = 4.7 Hz), 156.1 (d, *J* = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 0.45. IR (ATR): 1590 m, 1471 w, 1432 s, 1329 m, 1281 s, 1239 m, 1209 s, 1161 m, 1146 m, 1108 w, 1087 m, 1051 m, 919 w, 893 w, 866 m, 848 w, 794 w, 768 m, 743 s, 727 s, 710 m, 696 s. MS m/z (% relative intensity): 343 (24), 342 (M^+, 100), 341 (47), 266 (12), 265 (71), 249 (32), 218 (32), 189 (15). HRMS (EI): Calcd for $C_{22}H_{15}O_2P$ 342.0810, found: 342.0809.

2-Methoxy-10-phenyl-10*H*-phenoxaphosphinine 10-oxide (24).



White solid. (0.11 g, 72%). Mp = 180 °C. Rf 0.54 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 0.86 (t, *J* = 6.6 Hz, 3H), 1.24-1.39 (m, 10H), 1.87 (quint, *J* = 7.3 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 7.20-7.27 (m, 3H), 7.34-7.46 (m, 6H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.70 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.81 (dd, *J* = 13.0, 7.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 14.0, 22.5, 27.2, 28.6, 29.1, 29.3, 31.7, 43.3, 96.6 (d, *J* = 6.7 Hz), 105.9 (d, *J* = 108.3 Hz), 108.7, 115.6 (d, *J* = 102.5 Hz), 118.0 (d, *J* = 5.7 Hz), 120.0, 120.5, 120.7 (d, *J* = 12.5 Hz), 122.1, 123.4 (d, *J* = 5.7 Hz), 123.7 (d, *J* = 10.5 Hz), 126.3, 128.4 (d, *J* = 12.5 Hz), 131.1 (d, *J* = 5.8 Hz), 131.3, 131.4 (d, *J* = 6.7 Hz), 133.4, 135.1 (d, *J* = 115.9 Hz), 141.5, 143.9, 154.4 (d, *J* = 4.8 Hz), 155.9 (d, *J* = 2.9 Hz). ^{31}P NMR (CDCl$_3$, 161.83 MHz) δ: 1.6. IR (ATR): 2923 w, 2851 w, 1636 w, 1597 m, 1493 w, 1469 m, 1424 s, 1381 w, 1351 m, 1327 m, 1268 m, 1251 m, 1199 s, 1156 m, 1115 s, 1093 m, 1054 w, 1019 w, 984 w, 893 w, 822 m, 765 m, 742 s, 720 s, 695 s, 664 m. MS m/z (% relative intensity): 494 (34), 493 (M$^+$, 100), 395 (22), 394 (76), 277 (14). HRMS (EI): Calcd for $C_{32}H_{32}NO_2P$ 493.2171, found: 493.2168.

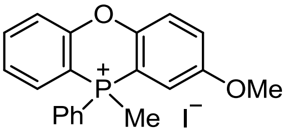
5-Methyl-10-phenyl-5,10-dihydrophenophosphazinine 10-oxide (25).



White solid. (78 mg, 86%). Mp = 162 °C. Rf 0.20 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.64 (s, 3H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 8.6, 5.8 Hz, 2H), 7.37 (t, *J* = 6.8 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.60 (dd, *J* = 12.4, 8.0 Hz, 2H), 7.77 (dd, *J* =

13.2, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 36.7, 115.1 (d, *J* = 6.6 Hz), 116.3 (d, *J* = 102.5 Hz), 121.2 (d, *J* = 10.6 Hz), 128.2 (d, *J* = 12.5 Hz), 131.2 (d, *J* = 10.6 Hz), 131.3 (d, *J* = 10.6 Hz), 131.4, 132.6, 133.7 (d, *J* = 111.1 Hz), 145.6 (d, *J* = 3.8 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 7.1. IR (ATR): 3446 w, 1586 m, 1454 m, 1441 s, 1340 m, 1250 w, 1171 s, 1147 m, 1119 m, 1089 m, 1043 w, 996 w, 871 m, 756 s, 736 m, 718 m, 707 s, 694 s. MS m/z (% relative intensity): 306 (20), 305 (M^+, 100), 304 (45), 228 (40), 227 (19), 212 (12), 181 (11), 180 (27), 152 (13), 91 (10), 77 (10). HRMS (EI): Calcd for $C_{19}H_{16}NOP$ 305.0970, found: 305.0973.

2-Methoxy-10-methyl-10-phenyl-10*H*-phenoxaphosphinin-10-ium iodide (26).

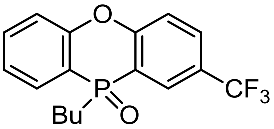


9 (0.13 g, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), $(Me_3Si)_3SiH$ (90 mg, 0.11 mL, 0.36 mmol) and DMF (0.6 mL) under a gentle stream of nitrogen. The vessel was heated at 130 °C for 12 h followed by cooling. To the reaction mixture, MeI (64 mg, 0.028 mL, 0.45 mmol) was added under a gentle stream of nitrogen, and the mixture was stirred at 100 °C for 20 h. After cooling to room temperature, the solvent was evaporated in vacuo, and the residue was purified by flash chromatography (CH_2Cl_2/MeOH) to give 2-methoxy-10-methyl-10-phenyl-10*H*-phenoxaphosphinin-10-ium iodide (**26**, 87 mg, 65%) as a white solid.

White solid (87 mg, 65%). Mp = 226 °C. Rf 0.26 (CH_2Cl_2/MeOH = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.45 (d, *J* = 13.6 Hz, 3H), 4.00 (s, 3H), 7.37 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.45 (dd, *J* = 9.0, 7.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.57-7.67 (m, 3H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.85 (t, *J* = 7.8 Hz, 1H), 8.06-8.15 (m, 3H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 14.1 (d, *J* = 57.5 Hz), 58.2, 99.0 (d, *J* = 91.1 Hz), 99.6 (d, *J* = 90.1 Hz), 112.4 (d, *J* = 8.6 Hz), 119.2 (d, *J*

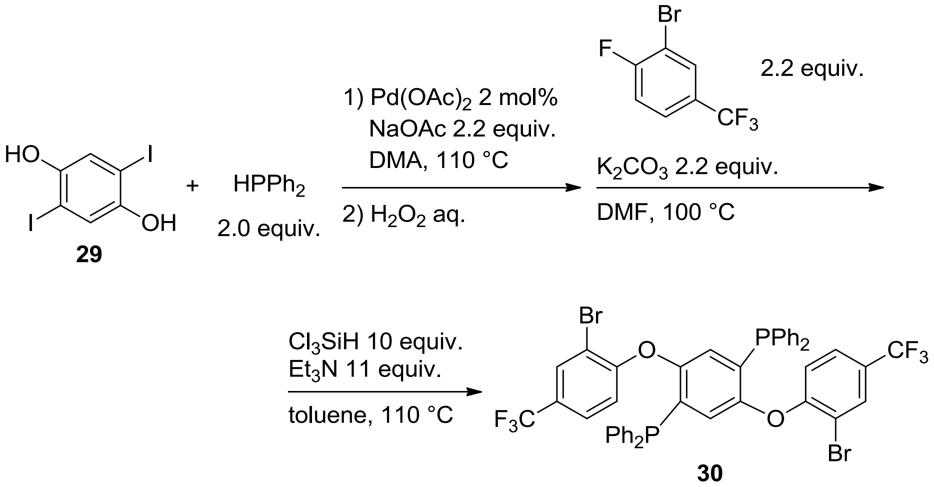
= 5.7 Hz), 120.9 (d, *J* = 7.6 Hz), 121.6 (d, *J* = 91.1 Hz), 125.9 (d, *J* = 11.6 Hz), 126.3 (d, *J* = 1.9 Hz), 130.1 (d, *J* = 14.4 Hz), 132.3 (d, *J* = 7.6 Hz), 133.1 (d, *J* = 12.5 Hz), 134.9 (d, *J* = 2.9 Hz), 136.8, 149.1, 155.3, 157.2 (d, *J* = 13.4 Hz). ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -6.6. IR (ATR): 2930 w, 2869 w, 2194 w, 1491 m, 1469 m, 1439 m, 1402 w, 1323 w, 1277 m, 1248 m, 1218 m, 1135 m, 1113 m, 1094 w, 1077 m, 1027 m, 911 s, 857 m, 844 m, 724 s, 688 m. HRMS (FAB): Calcd for $C_{20}H_{18}O_2P$ $[M-I]^+$ 321.1039, found: 321.1041.

10-Butyl-2-(trifluoromethyl)-10*H*-phenoxaphosphinine 10-oxide (28).



Colorless oil (49 mg, 48%). Rf 0.49 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.80 (t, *J* = 6.6 Hz, 3H), 1.23-1.31 (m, 4H), 2.08-2.14 (m, 2H), 7.33 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.37-7.43 (m, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.97 (dd, *J* = 12.2, 7.8 Hz, 1H), 8.25 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 13.3, 23.6 (d, *J* = 17.3 Hz), 23.7, 33.9 (d, *J* = 79.5 Hz), 114.4 (d, *J* = 96.7 Hz), 115.5 (d, *J* = 93.9 Hz), 118.3 (d, *J* = 5.8 Hz), 119.0 (d, *J* = 4.7 Hz), 123.4 (quart, *J* = 272.1 Hz), 124.7, 124.8, (d, *J* = 3.8 Hz), 126.4 (quart d, *J* = 34.1, 9.8 Hz), 128.2, 130.4, 134.0, 154.6, 157.1. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: 9.0. IR (ATR): 3445 w, 2961 w, 2934 w, 2872 w, 1620 w, 1602 m, 1469 m, 1440 m, 1408 w, 1328 s, 1270 s, 1227 m, 1166 s, 1122 s, 1090 s, 1073 m, 898 w, 844 m, 761 m, 738 w, 700 w, 655 w. MS m/z (% relative intensity): 340 (M^+, 34), 299 (13), 298 (84), 284 (27), 283 (100), 217 (18). HRMS (EI): Calcd for $C_{17}H_{16}F_3O_2P$ 340.0840, found: 340.0839.

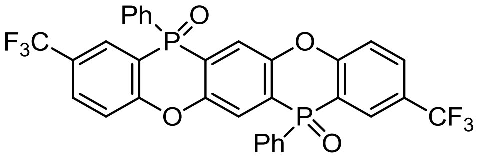
(2,5-Bis(2-bromo-4-(trifluoromethyl)phenoxy)-1,4-phenylene)bis(diphenylphosphine) (30).



A mixture of 2,5-diiodobenzene-1,4-diol[13] (3.0 g, 8.2 mmol), diphenylphosphine (2.9 mL, 17 mmol), $Pd(OAc)_2$ (37 mg, 0.16 mmol) and NaOAc (1.5 g, 18 mmol) in anhydrous DMA (30 mL) under nitrogen was stirred at 110 °C for 16 h. The reaction mixture was then filtered through a pad of celite with EtOAc. The filtrate was washed with water (50 mL×3) and dried over $MgSO_4$. The solvent was removed in vacuo to give a pale yellow oil (4.5 g), which was then dissolved in THF (75 mL) and MeOH (75 mL). An aqueous solution of H_2O_2 (ca. 30%, a couple of drops) was then added to the THF/MeOH solution. After stirring at room temperature for 6 h, the solvent was removed under reduced pressure to give a residue, which was then purified by column chromatography to give (2,5-dihydroxy-1,4-phenylene)bis(diphenylphosphine oxide) as a pale yellow solid (3.9 g, 7.6 mmol). A 200 mL three-necked flask was charged with crude (2,5-dihydroxy-1,4-phenylene)bis(diphenylphosphine oxide) (3.9 g, 7.6 mmol), 2-bromo-1-fluoro-4-(trifluoromethyl)benzene (4.0 g, 17 mmol, purchased from TCI), K_2CO_3 (2.3 g, 17 mmol), and DMF (32 mL) at 100° C for 48 h. The mixture was allowed to cool to room temperature and filtered through a pad of celite. The filtrate was poured into water, and the precipitate was extracted with ethyl acetate (80 mL×3). The combined organic extract was concentrated under vacuum to give a yellow solid, which was washed with (EtOAc/CH_2Cl_2) to give (2,5-bis(2-bromo-4-(trifluoromethyl)phenoxy)-1,4-phenylene)bis(diphenylphosphine oxide) as a white solid (2.3 g, 29% over three steps). A solution of the obtained bis(diphosphine oxide) (2.3 g, 2.4 mmol) in toluene (30 mL) was frozen using an EtOH/liquid nitrogen bath, to which trichlorosilane (2.4 mL, 24 mmol) and triethylamine (3.7 mL, 26 mmol) were added. The mixture was stirred at 110 °C under nitrogen for 12 h. After cooling to room temperature, sat. $NaHCO_3$ aq. (2 mL) was added, and the mixture was stirred for 5 min. The mixture was filtered through a pad of alumina and evaporated in vacuo to give a residue, which was purified by flash chromatography (hexane/EtOAc = 10/1) to give **30** as a white solid (0.66 g, 30%).

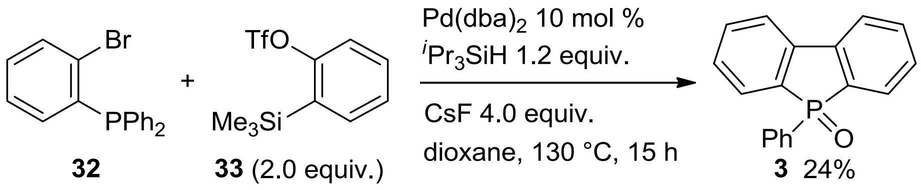
White solid. Mp = 206 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.16 (t, *J* = 4.0 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 2H), 7.24-7.27 (m, 20H), 7.66 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 114.3, 118.6, 123.0, 123.1 (quart, *J* = 272.1 Hz), 125.4 (d, *J* = 2.9 Hz), 125.5, 126.6 (quart, *J* = 33.5 Hz), 128.2, 128.5 (d, *J* = 7.7 Hz), 129.2, 130.8 (quart, *J* = 2.9 Hz), 132.2 (d, *J* = 20.1 Hz), 133.9 (d, *J* = 21.1 Hz), 134.5 (d, *J* = 9.6 Hz), 135.7, 131.5, 153.2 (d, *J* = 16.3 Hz), 155.6. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -16.0. IR (ATR): 1607 w, 1492 w, 1443 m, 1404 w, 1346 w, 1320 s, 1259 s, 1233 m, 1159 s, 1111 s, 1075 s, 1046 m, 889 w, 813 m, 744 s, 694 s. MS m/z (% relative intensity, FAB): 941 (11), 925 (M^++3, 6), 923 (M^++1, 3), 861 (16), 859 (12), 845 (16), 843 (13), 307 (20), 289 (12), 201 (19), 185 (11), 183 (23), 155 (24), 154 (100), 139 (11), 138 (247), 137 (51), 136 (70), 120 (11), 107 (20), 91 (13), 90 (14), 89 (21), 77 (20). HRMS (FAB): Calcd for $C_{44}H_{29}Br_2F_6O_2P_2$ 922.9914, Found 922.9906.

7,14-Diphenyl-7,14-dihydrobenzo[5,6][1,4]oxaphosphinino[2,3-*b*]phenoxaphosphinine 7,14-dioxide (31).



White solid. (66 mg, 69%). Mp = 361 °C. Rf 0.57 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.45 (dd, *J* = 8.6, 5.0 Hz, 2H), 7.51 (t, *J* = 6.2 Hz, 4H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.59-7.66 (m, 4H), 7.79-7.84 (m, 4H), 8.02 (d, *J* = 12.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.1 (d, *J* = 102.5 Hz), 119.4 (d, *J* = 5.7 Hz), 121.1 (t, *J* = 6.2 Hz), 122.2 (d, *J* = 97.7 Hz), 123.2 (quart, *J* = 271.1 Hz), 127.0 (quart d, *J* = 33.5, 10.5 Hz), 128.9 (quart, *J* = 3.5 Hz), 129.1 (d, *J* = 13.4 Hz), 131.2, 131.4 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 121.6 Hz), 132.9 (d, *J* = 1.9 Hz), 150.8 (d, *J* = 16.3 Hz), 157.2. ^{31}P NMR ($CDCl_3$, 161.83 MHz) δ: -1.1. IR (ATR): 1739 w, 1619 w, 1457 w, 1380 s, 1328 m, 1279 m, 1214 s, 1158 m, 1119 s, 1089 s, 890 w, 836 m, 749 m, 720 m, 690 s, 667 s. MS m/z (% relative intensity): 643 (35), 642 (M^+, 100), 641 (42), 565 (28), 559 (13), 549 (12), 321 (11). HRMS (EI): Calcd for $C_{32}H_{18}F_6O_4P_2$ 642.0585, found: 642.0586.

Intermolecular assembly of dibenzophosphole via catalytic C-P bnod cleavage (Scheme 2.6)



An oven-dried 5 mL screw-capped vial was charged with (2-bromophenyl)diphenylphosphine (**32**, 0.10 g, 0.30 mmol), CsF (0.18 g, 1.2 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**33**, 0.18 g, 0.60 mmol), ${}^{i}Pr_3SiH$ (57.0 mg, 74 μL, 0.36 mmol), toluene (1 mL) and CH_3CN (0.1 mL) under a gentle stream of nitrogen. The vessel was heated at 130 °C for 12 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by flash chromatography (EtOAc) to give 5-phenyl-5*H*-benzophosphole 5-oxide (**3**, 20 mg, 24%) as a white solid.

2.5 References and Notes

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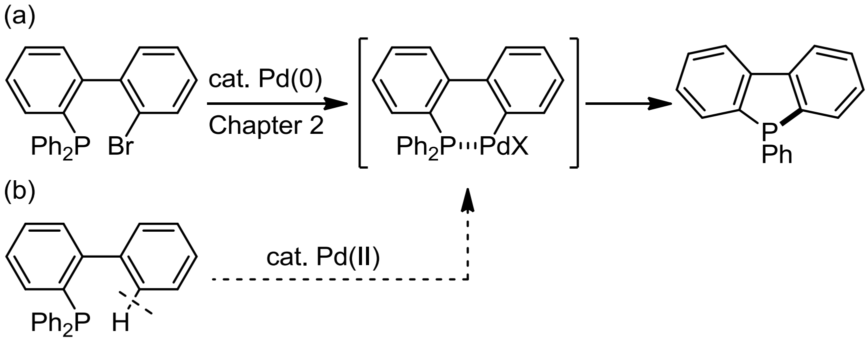
Chapter 3

Palladium-Catalyzed Direct Synthesis of Phosphole Derivatives from Triarylphosphines through Cleavage of Carbon‐Hydrogen and Carbon‐Phosphorus Bonds

3.1 Introduction

In Chapter 2, the Pd-catalyzed synthesis of phosphole derivatives using triarylphosphine was described (Scheme 3.1a). This reaction features C-P bond cleavage, which allows for the use of tertiary phosphines as stable and readily available phosphorus sources. However, since the starting material contains both a phosphino group and a bromo group, its synthesis is difficult, so the scope of substrates is still limited. It should be noted that the preparation of a six-membered palladacycle having a structure similar to the intermediate in Chapter 2 has been reported through the stoichiometric cleavage of a C-H bond.[1] We therefore envisioned that the reaction of simple biphenylphosphine in the presence of a Pd(II) catalyst would form the six-membered palladacycle intermediate via C-H bond cleavage, and then produce the desired phosphole through C-P bond cleavage, similar to the reaction in Chapter 2 (Scheme 3.1b).

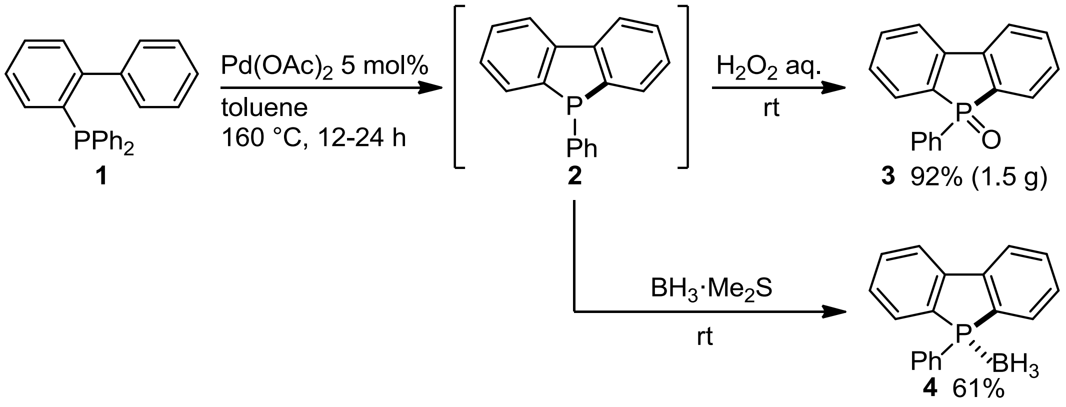
Scheme 3.1. The Synthesis of Phospholes through the Cleavage of C-H and C-P Bond



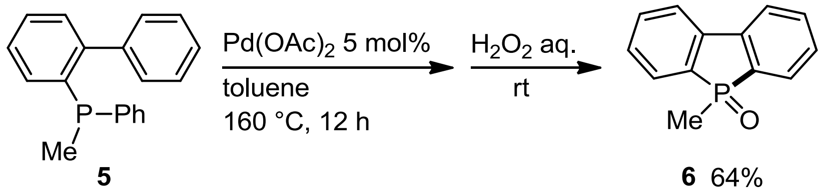
3.2 Results and Discussion

After several experiments, the expected reaction was found to occur by mixing **1** with a catalytic quantity of $Pd(OAc)_2$ at 160 °C (Scheme 3.2). Since the generated phosphole **2** is susceptible to oxidation upon workup, the product was isolated as oxide **3** by treatment with aqueous H_2O_2. Alternatively, complexation with BH_3 afforded **4** as a stable and crystalline solid. It should be noted that this protocol can be conducted on the gram scale without any modification (1.5 g of **3** were synthesized successfully).

Scheme 3.2. Pd-Catalyzed Synthesis of Phosphole Derivatives through the Cleavage of C-H and C-P bonds



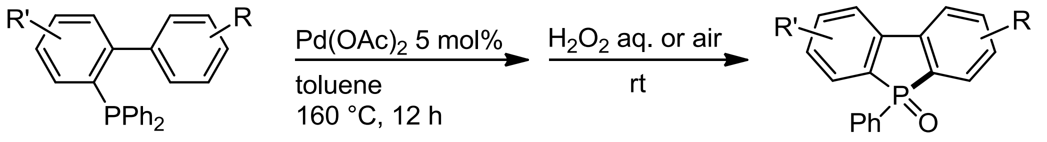
A biphenyl bearing a PMePh group, as in **5**, underwent palladium-catalyzed cyclization to deliver P-alkyl phosphole oxide **6** via exclusive cleavage of a P-Ar bond rather than a P-Me bond (eq. 3.1).[2]

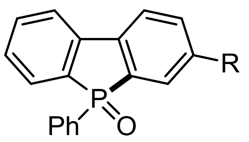


(3.1)

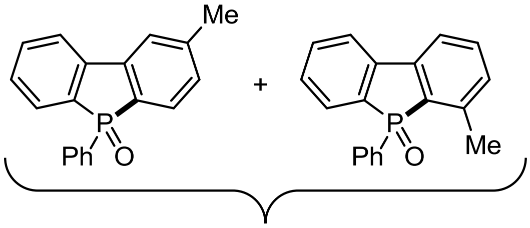
This operationally trivial protocol was successfully applied to the synthesis of a diverse array of phospholes (Table 3.1). The high functional group tolerance allows access to a range of electronically different phospholes bearing ether **8** and **24**, amine **9** and **17**, ester **10**, ketone **11**, nitrile **12**, and fluoride **13** groups.

Table 3.1. Scope of Substrates[a]

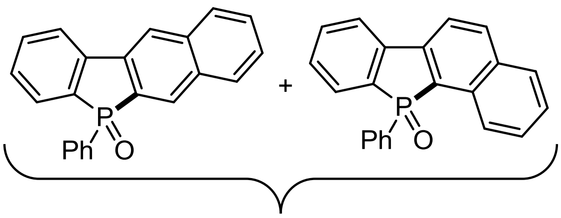




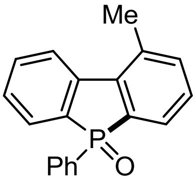
R = H (**3**)	80%	Ac (**11**)	72%
Bu (**7**)	94%	CN (**12**)	84%
OMe (**8**)	77%	F (**13**)	62%
NMe_2 (**9**)	69%	Cl (**14**)	92%
CO_2Me (**10**)	64%	Br (**15**)	67%



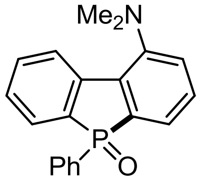
81% (**18**:**19** = 10:1)



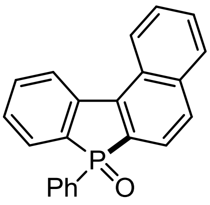
67% (**20**:**21** = 2.8:1)



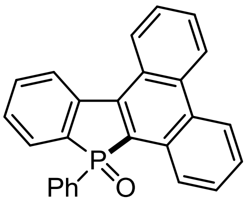
16 54%



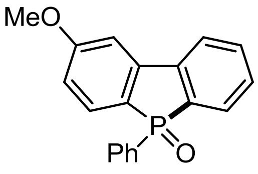
17 77%



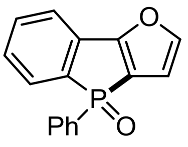
22 94%



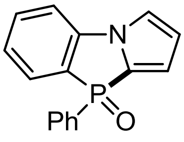
23 58%



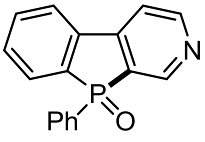
24 75%



25 54%



26 58%[b]

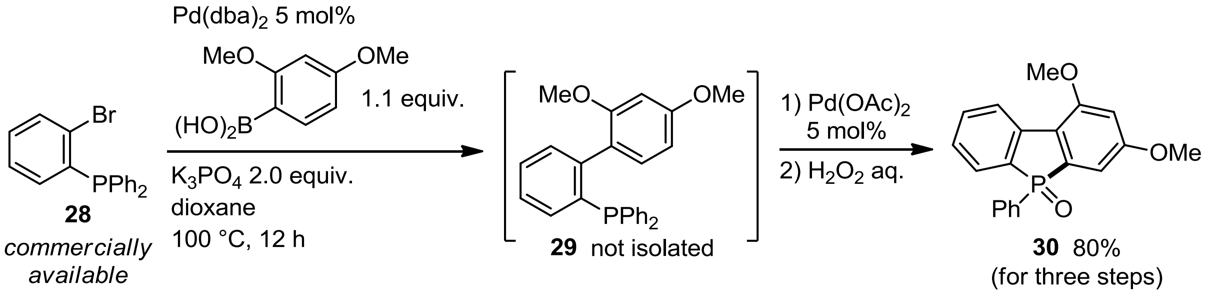


27 85%

[a] Reaction conditions: biarylphosphine (0.30 mmol), Pd(OAc)$_2$ (0.015 mmol) and toluene (1 mL) in a sealed tube at 160 °C, for 12 h. Isolated yields are shown. [b] The reaction was set up in a glovebox because of the sensitivity of the starting phosphine to oxygen.

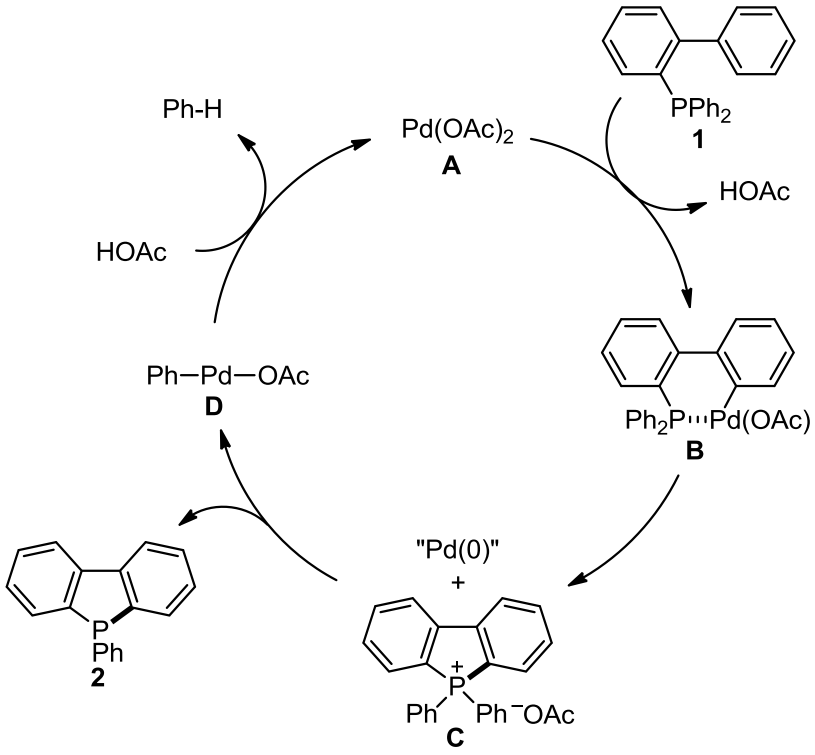
The compatibility of chlorides and bromides, as in **14** and **15**, which can serve as handles for further structural modification of the phosphole skeleton is particularly useful (see Scheme 3.6). C-P bond formation can occur smoothly with substrates bearing an *ortho*-substituent to deliver 1-substituted dibenzophospholes, as in **16** and **17**. Substrates bearing a *meta*-substituent underwent cyclization at the less hindered site regioselectively to form **18** as the major product. The starting biarylphosphines used in this study are readily accessible. Some of them are commercially available ligands (i.e., **17** is derived from a ligand known as PhDavePhos[3]). The modularity of this protocol enables various π-systems, including naphthalenes **20-22**, phenanthrenes **23**, furans **25**, pyrroles **26**, and pyridines **27**, to be incorporated into the phosphole framework. Others can be rapidly prepared from commercially available (2-bromophenyl)diphenylphosphine (**28**) via a cross-coupling reaction, and the subsequent phosphole formation can be performed without isolation of the biarylphosphine intermediate **29** (Scheme 3.3).

Scheme 3.3. Synthesis of Phosphole **30** from **28**



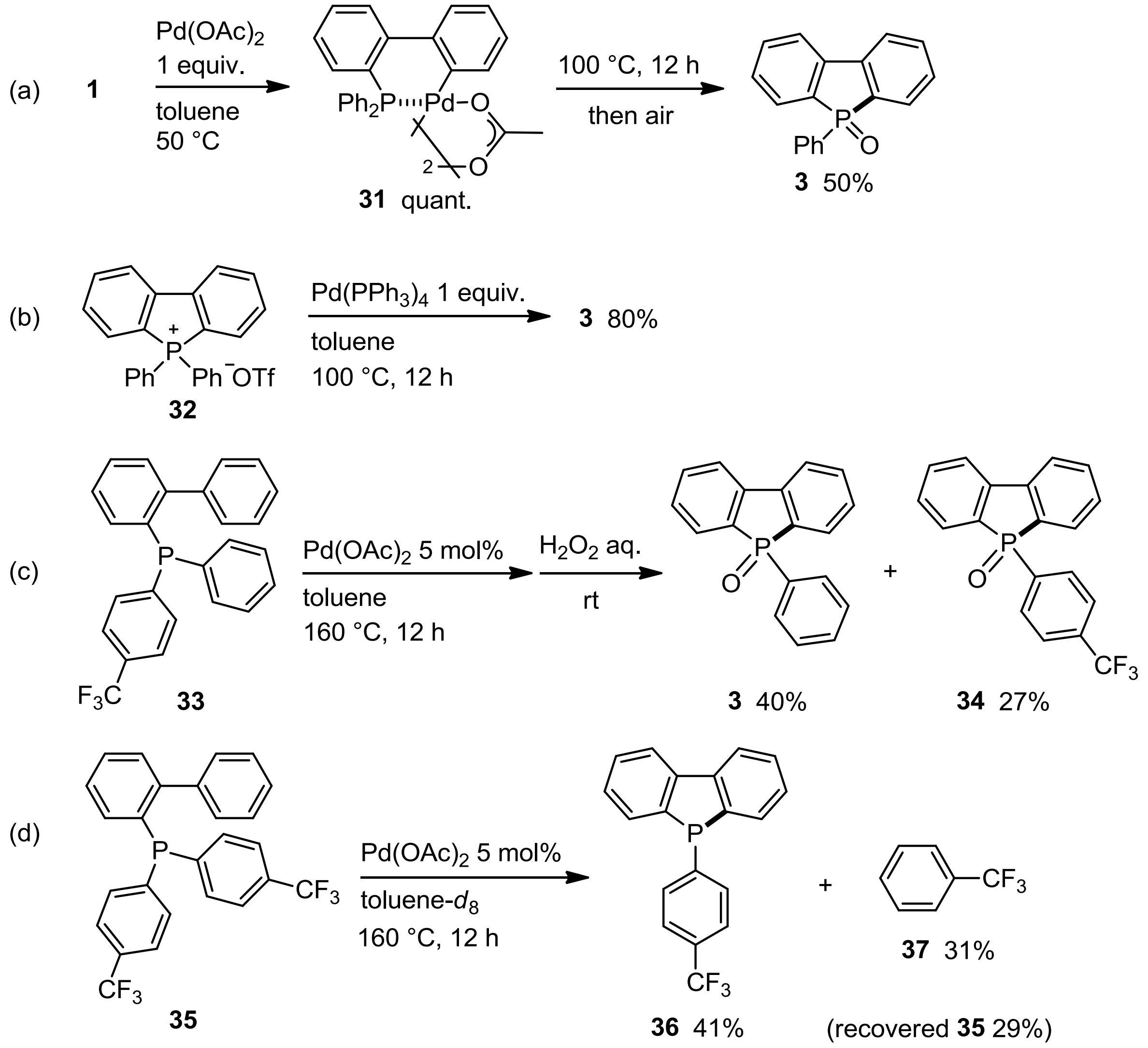
A possible mechanism is depicted in Scheme 3.4. The reaction is initiated by the reaction of Pd(II) with **1** to form the cyclopalladated complex **B**.[1] Reductive elimination from **B** subsequently leads to the formation of phosphonium **C** along with Pd(0).[4] The phosphonium **C** immediately undergoes oxidative addition to Pd(0), which is in close proximity, to provide phosphole **2** and PhPd(OAc) (**D**) via cleavage of a C-P bond.[5] Finally, PhPd(OAc) is protonated with AcOH, which is released in the initial cyclometallation step, to regenerate $Pd(OAc)_2$.[6]

Scheme 3.4. A Plausible Mechnism



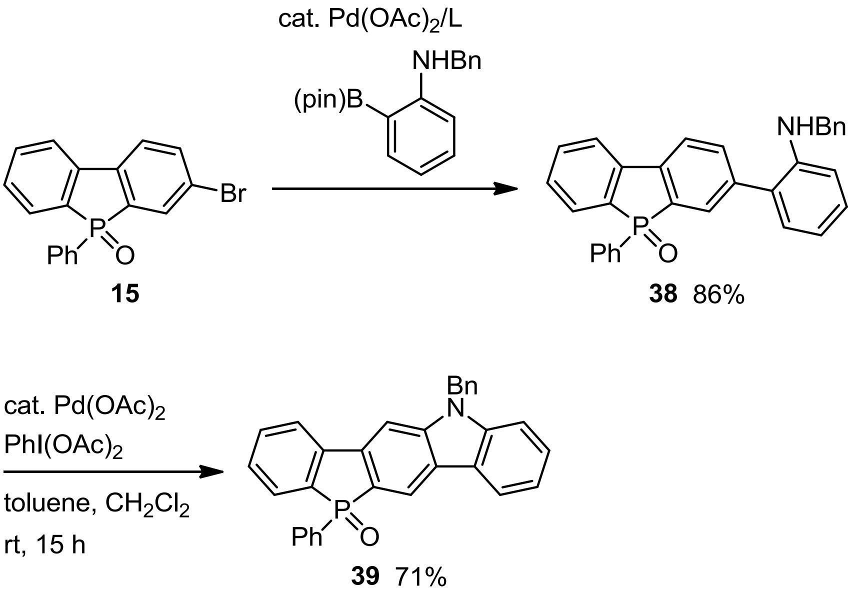
Several experimental results that support our proposed mechanism were obtained (Scheme 3.5). First, cyclopalladated complex **B** could indeed be synthesized by the reaction of **1** with 1 equiv of $Pd(OAc)_2$ at 50 °C. X-ray crystallographic analysis revealed that the complex was formed as a dimer **31** (Scheme 3.5a). Heating a solution of **31** in toluene at 100 °C afforded phosphole **3**, suggesting that the metallacycle **31** serves as a plausible intermediate in the catalytic cycle.[7] Second, the potential intermediacy of phosphonium salt **C** in the C-P bond cleavage process was confirmed. The reaction of independently synthesized **32** with $Pd(PPh_3)_4$ at 100 °C led to the formation of phosphole **3** (Scheme 3.5b). This mechanistic scenario is also consistent with the observation of cyclization of **33**, in which a more electron-deficient aryl group on the phosphorus was eliminated preferentially over a phenyl group (Scheme 3.5c).[8] Third, the fate of the cleaved aryl group was determined to be the corresponding arene, as is proposed in Scheme 3.4, by examining the reaction of **35** (Scheme 3.5d).

Scheme 3.5. Mechanistic Studies.



The functionalized phospholes obtained in the present study are amenable to further elaboration. For example, the Suzuki-Miyaura reaction of bromophosphole **15** followed by catalytic C-H amination[9] enables rapid assembly of the extended π-conjugated molecule **39** (Scheme 3.6).

Scheme 3.6. Synthetic Elaboration of **16**.



3.3 Conclusion

A palladium-catalyzed method for the synthesis of phospholes from triarylphosphines has been developed. Synthetic advantages over previously reported methods includes 1) operational simplicity, 2) direct use of simple starting materials, 3) excellent functional group compatibility, and 4) high modularity of the aromatic component to be incorporated. These features enable rapid access to a structurally diverse array of phosphorus-based π-systems, the physical properties of which are of significant interest.

3.4 Experimental Section

General Information.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a JEOL ECS-400 spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ with H_3PO_4 as the internal standard using a JEOL ECS-400 spectrometer. The data are given as follows: chemical shifts δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-DX303. Melting points were determined using a SRS MPA 100 instrument. Column chromatography was performed using SiO_2 [Silicycle SiliaFlash F60 (230-400 mesh)]. Some compounds were purified using HPLC LC9210NEXT. Fluorescence spectra were recorded using Shimadzu RF-5300 PC spectrofluorophotometer. X-ray crystallographic structure analysis was performed with Rigaku R-AXIS RAPID diffractometer using graphite-monochromated Mo-Kα radiation.

Materials.

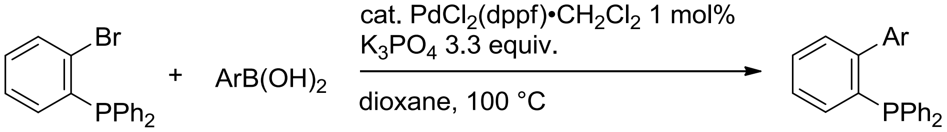
Unless otherwise noted, all reagents were obtained from commercial suppliers and were used as received. $Pd(OAc)_2$ and 2-(dimethylamino)-2'-(diphenylphosphino)biphenyl (CAS: 240417-00-9) was purchased from Wako Pure Chemical Industries, Ltd. Toluene was dried on a glass contour solvent-dispensing system (Nikko Hansen & Co., Ltd.). 2-Diphenylphosphino biphenyl (**1**, CAS: 13885-09-1)[10] and

[1,1'-biphenyl]-2-yl(methyl)(phenyl)phosphine (**5**, CAS: 1064156-66-6)[11] were prepared according to the literature procedure.

Synthesis of Starting Materials

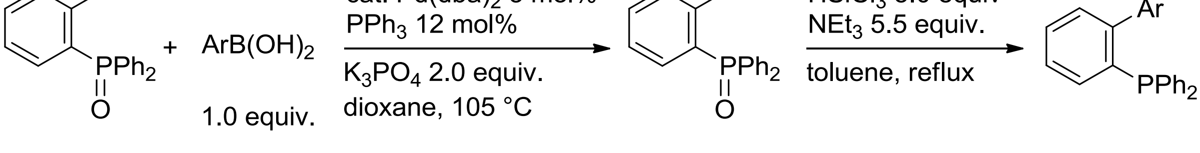
Unless otherwise noted, the substrates were prepared using the following two methods.

Method A:[12] **Suzuki-Miyaura coupling between (2-bromophenyl)diphenylphosphine and arylboronic acid**



The representative procedure is as follows. A two-necked flask was charged with (dppf)$PdCl_2 \cdot CH_2Cl_2$ (20 mg, 0.025 mmol), (2-bromophenyl)diphenylphosphine (1.7 g, 5.0 mmol), 4-methoxyphenylboronic acid (0.84 g, 5.6 mmol), anhydrous K_3PO_4 (3.5 g, 17 mmol) and dry 1,4-dioxane (55 mL). The reaction mixture was heated at 100 °C with vigorous stirring overnight. After cooling to room temperature, the reaction mixture was diluted with water (100 mL) and extracted with Et_2O (3×50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was purified by flash column chromatography (hexane/EtOAc = 10/1) to give pure 2-diphenylphosphino-4'-methoxybiphenyl (**SM-8**, 0.72 g, 39%) as a white solid.

Method B:[13] **Suzuki-Miyaura coupling between (2-bromophenyl)diphenylphosphine oxide and arylboronic acids and subsequent reduction**

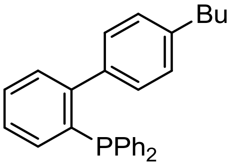


The representative procedure is as follows. A two-necked flask was charged with (2-bromophenyl)diphenylphosphine oxide (2.4 g, 6.8 mmol) and 4-cyanophenylboronic acid

(1.0 g, 6.8 mmol), together with Pd(dba)$_2$ (0.12 g, 0.20 mmol), PPh$_3$ (0.22 g, 0.82 mmol) and K_3PO_4 (2.9 g, 14 mmol) in 27 mL of dioxane under a nitrogen atmosphere. The reaction mixture was stirred at 105 °C for 12 h and cooled to room temperature. The mixture was diluted with water (50 mL) and extracted with $CHCl_3$ (3×30 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. After flash chromatography (EtOAc/hexane = 2/1), 2'-(diphenylphosphoryl)-4-cyanobipheny was obtained (1.6 g, 62%).

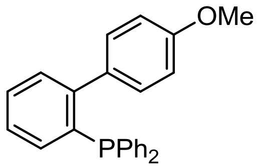
A solution of 2'-(diphenylphosphoryl)-4-cyanobipheny (1.6 g, 4.1 mmol) in toluene (40 mL) was frozen using an EtOH/liquid nitrogen bath, to which trichlorosilane (2.1 mL, 21 mmol) and triethylamine (3.2 mL, 23 mmol) were added. The mixture was stirred at 110 °C under nitrogen overnight. After cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ (5 mL) was added, and the mixture was stirred for 5 min. The mixture was filtered through a pad of alumina and evaporated in vacuo to give the crude product. Purification by flash chromatography (hexane/EtOAc = 10/1) gave 2-diphenylphosphino-4'-cyanobiphenyl as a white solid (**SM-12**, 0.66 g, 44%).

2-Diphenylphosphino-4'-butylbiphenyl (SM-7)



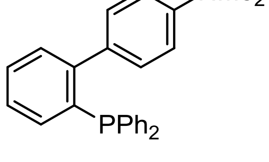
Method A was followed except that 4-butylphenylboronic acid was used instead of 4-methoxyphenylboronic acid. Colorless oil. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.88 (t, *J* = 7.4 Hz, 3H), 1.31 (sext, *J* = 7.4 Hz, 2H), 1.56 (quint, *J* = 7.6 Hz, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 7.00-7.29 (m, 18H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 13.9, 22.2, 33.3, 35.2, 126.9, 127.4, 128.1, 128.2, 128.5, 129.4 (d, *J* = 2.9 Hz), 130.0 (d, *J* = 4.7 Hz), 133.7 (d, *J* = 20.2 Hz), 133.9, 135.6 (d, *J* = 14.4 Hz), 137.6 (d, *J* = 12.5 Hz), 138.8 (d, *J* = 5.7 Hz), 141.4, 148.1 (d, *J* = 28.8 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: -12.7. IR (ATR): 3050 w, 2955 w, 2927 w, 2856 w, 1584 w, 1514 w, 1477 w, 1460 w, 1433 m, 1407 w, 1378 w, 1306 w, 1248 w, 1183 w, 1159 w, 1116 w, 1090 w, 1004 w, 911 w, 834 w, 762 m, 742 s, 695 s. MS, *m/z* (relative intensity, %): 394 (M^+, 43), 393 (M^+-1, 100), 350 (19). Exact Mass (EI, 17 eV): Calcd for $C_{28}H_{27}P$ 394.1850, found 394.1849.

2-Diphenylphosphino-4’-methoxybiphenyl (SM-8) [CAS: 875783-59-8]



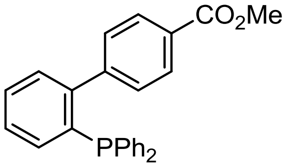
Synthesized by Method A. White solid. Mp = 140 °C, Rf 0.34 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.79 (s, 3H), 6.79 (d, *J* = 8.4 Hz, 2H), 7.03 (dd, *J* = 7.4, 3.7 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.19-7.32 (m, 12H), 7.37 (td, *J* = 7.5, 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.2, 112.9, 127.0, 128.26, 128.34, 128.6, 130.2 (d, *J* = 4.8 Hz), 130.7 (d, *J* = 3.8 Hz), 133.8 (d, *J* = 20.1 Hz), 134.08, 134.13, 135.8 (d, *J* = 13.4 Hz), 137.7 (d, *J* = 11.6 Hz), 147.9 (d, *J* = 28.8 Hz), 158.7. ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -13.3. IR (ATR): 3060 w, 2832 w, 1604 w, 1511 m, 1474 w, 1459 w, 1432 m, 1292 w, 1239 m, 1173 m, 1106 w, 1086 w, 1068 w, 1033 m, 998 w, 919 w, 839 m, 806 m, 762 m, 743 s, 697 s, 661 w. MS, *m/z* (relative intensity, %): 368 (M^+, 42), 367 (M^+-1, 100). Exact Mass (EI, 18 eV): Calcd for $C_{25}H_{21}OP$ 368.1330, found 368.1327.

2-Diphenylphosphino-4’-dimethylaminobiphenyl (SM-9)



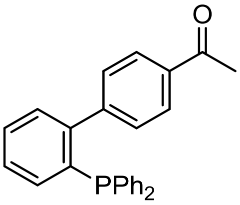
Method B was followed except that (4-dimethylamino)phenylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 145 °C. Rf 0.23 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 2.94 (s, 6H), 6.63 (d, *J* = 8.8 Hz, 2H), 7.04 (dd, *J* = 11.0, 3.8 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 7.18-7.30 (m, 11H), 7.34-7.36 (m, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 40.5, 111.5, 126.6, 128.2, 128.3, 128.6, 129.8 (d, *J* = 6.6 Hz), 130.2 (d, *J* = 4.8 Hz), 130.4 (d, *J* = 3.8 Hz), 133.8 (d, *J* = 19.2 Hz), 134.4, 135.5 (d, *J* = 13.4 Hz), 138.3 (d, *J* = 12.5 Hz), 148.7 (d, *J* = 29.7 Hz), 149.6. ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.6. IR (ATR): 3038 w, 2803 w, 1609 m, 1523 m, 1477 m, 1457 m, 1432 m, 1355 m, 1261 w, 1225 m, 1195 m, 1166 m, 1091 m, 1069 m, 1027 m, 998 w, 944 w, 821 s, 766 s, 743 s, 694 s. MS, *m/z* (relative intensity, %): 381 (M^+, 47), 380 (M^+-1, 100), 366 ((M^+-15, 11), 364 (24), 190 (10). Exact Mass (EI, 18 eV): Calcd for $C_{26}H_{24}NP$ 381.1646, found 381.1648.

Methyl 2'-(diphenylphosphino)-[1,1'-biphenyl]-4-carboxylate (SM-10)



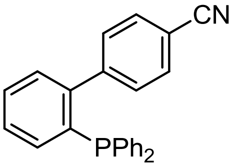
Method A was followed except that 4-(methoxycarbonyl)phenylboronic acid was used instead of 4-methoxyboronic acid. White solid. Mp = 146 °C. Rf 0.23 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.90 (s, 3H), 7.06-7.08 (m, 1H), 7.18-7.22 (m, 4H), 7.24-7.30 (m, 10H), 7.38-7.42 (m, 1H), 7.92 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 52.0, 127.8, 128.4 (d, *J* = 6.6 Hz), 128.6, 128.7, 128.9, 129.7 (d, *J* = 3.9 Hz), 129.8, 133.8 (d, *J* = 20.1 Hz), 134.1, 135.8 (d, *J* = 15.4 Hz), 137.1 (d, *J* = 11.6 Hz), 146.4 (d, *J* = 5.7 Hz), 146.9, 147.2, 167.0. ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.2. IR (ATR): 1717 s, 1610 w, 1476 w, 1456 w, 1432 m, 1400 w, 1310 w, 1274 s, 1188 m, 1116 m, 1069 w, 1024 w, 1003 w, 968 w, 84 m, 828 w, 778 w, 748 s, 694 s. MS, *m/z* (relative intensity, %): 396 (M^+, 40), 395 (M^+-1, 100). Exact Mass (EI, 18 eV): Calcd for $C_{26}H_{21}O_2P$ 396.1279, found 396.1269.

2-Diphenylphosphino-4’-acetylbiphenyl (SM-11)



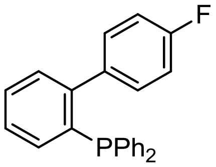
Method B was followed except that 4-acetylphenylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 132 °C. Rf 0.14 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 2.58 (s, 3H), 7.06-7.09 (m, 1H), 7.18-7.23 (m, 4H), 7.28-7.30 (m, 10H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 26.6, 127.6, 127.9, 128.4 (d, *J* = 7.6 Hz), 128.6, 128.8, 129.8 (d, *J* = 4.7 Hz), 129.9 (d, *J* = 3.8 Hz), 133.8 (d, *J* = 19.2 Hz), 134.2, 135.6, 135.8, 137.0 (d, *J* = 11.6 Hz), 146.6 (d, *J* = 5.8 Hz), 146.9 (d, *J* = 28.8 Hz), 197.7. ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.3. IR (ATR): 3047 w, 1677 s, 1602 w, 1582 w, 1477 w, 1457 w, 1433 m, 1401 w, 1356 m, 1307 w, 1263 s, 1184 w, 1157 w, 1092 w, 1068 w, 1025 w, 1002 w, 956 w, 850 w, 834 s, 743 s, 693 s. MS, *m/z* (relative intensity, %): 380 (M$^+$, 41), 379 (M$^+$-1, 100), 337 (10), 336 (11). Exact Mass (EI): Calcd for $C_{26}H_{21}OP$ 380.1330, found 380.1323.

2-Diphenylphosphino-4’-cyanobiphenyl (SM-12)



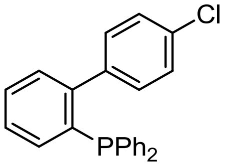
Synthesized by Method B. White solid. Mp = 120 °C. Rf 0.23 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.05-7.07 (m, 1H), 7.16-7.21 (m, 4H), 7.23-7.34 (m, 10H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 110.9, 118.9, 128.2, 128.5 (d, *J* = 6.7 Hz), 128.78, 128.84, 129.7 (d, *J* = 3.8 Hz), 130.4 (d, *J* = 3.8 Hz), 131.3, 133.9 (d, *J* = 20.1 Hz), 136.0 (d, *J* = 15.4 Hz), 136.5 (d, *J* = 10.6 Hz), 145.8, 146.1, 146.4 (d, *J* = 5.7 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -12.8. IR (ATR): 3065 w, 2230 w, 1607 w, 1584 w, 1476 w, 1461 w, 1433 m, 1400 w, 1309 w, 1250 w, 1180 w, 1159 w, 1090 w, 1072 w, 1026 w, 1005 w, 973 w, 920 w, 842 m, 769 m, 745 s, 697 s. MS, *m/z* (relative intensity, %): 363 (M^+, 42), 362 (M^+-1, 100), 208 (11). Exact Mass (CI): Calcd for $C_{25}H_{18}NP+H^+$ 364.1255, found 364.1259.

2-Diphenylphosphino-4'-fluorobiphenyl (SM-13)



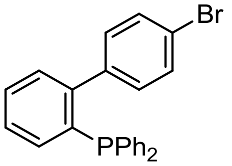
Method B was followed except that 4-fluorophenylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 127 °C. Rf 0.46 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.91 (t, *J* = 8.6 Hz, 2H), 7.02-7.05 (m, 1H), 7.10-7.13 (m, 2H), 7.20-7.22 (m, 4H), 7.24-7.28 (m, 7H), 7.36 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 114.4 (d, *J* = 21.1 Hz), 127.5, 128.4 (d, *J* = 6.7 Hz), 128.5, 128.7, 130.1 (d, *J* = 4.7 Hz), 131.2 (q, *J* = 3.8 Hz), 133.86 (d, *J* = 20.1 Hz), 133.91, 136.1 (d, *J* = 14.4 Hz), 137.2 (d, *J* = 11.5 Hz), 137.5 (q, *J* = 3.9 Hz), 147.0 (d, *J* = 27.8 Hz), 162.0 (d, *J* = 246.3 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -12.9. IR (ATR): 3061 w, 1603 w, 1510 m, 1474 w, 1460 w, 1432 m, 1238 w, 1214 m, 1157 m, 1124 w, 1089 w, 1068 w, 1025 w, 1006 w, 835 s, 819 m, 761 m, 744 s, 696 s, 662 w. MS, *m/z* (relative intensity, %): 356 (M^+, 39), 355 (M^+-1, 100), 201 (12). Exact Mass (EI, 19 eV): Calcd for $C_{24}H_{18}FP$ 356.1130, found 356.1123.

2-Diphenylphosphino-4'-chlorobiphenyl (SM-14)



Method B was followed except that 4-chlorophenylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 115 °C. Rf 0.43 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.03-7.06 (m, 1H), 7.08-7.10 (m, 2H), 7.18-7.31 (m, 14H), 7.38 (td, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 127.6, 127.7, 128.4 (d, J = 6.6 Hz), 128.6, 128.7, 130.0 (d, J = 4.7 Hz), 131.0 (d, J = 3.8 Hz), 133.2, 133.9 (d, J = 20.1 Hz), 134.0, 135.9 (d, J = 14.4 Hz), 137.2 (d, J = 11.4 Hz), 140.0 (d, J = 6.7 Hz), 146.8 (d, J = 27.7 Hz). ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.2. IR (ATR): 3062 w, 1476 w, 1458 w, 1432 m, 1395 w, 1308 w, 1248 w. 1206 w, 1159 w, 1088 m, 1022 w, 1004 w, 920 w, 828 m, 743 s, 719 w, 697 s. MS, *m/z* (relative intensity, %): 374 (M$^+$+2, 13), 373 (M$^+$+1, 39), 372 (M$^+$, 39), 371 (M$^+$-1, 100), 259 (11), 257 (11). Exact Mass (EI, 18 eV): Calcd for C$_{24}$H$_{18}$ClP 372.0835, found 372.0840.

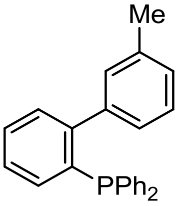
2-Diphenylphosphino-4'-bromobiphenyl (SM-15)



Method B was followed except that 4-bromophenylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 102 °C. Rf 0.43 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.02-7.04 (m, 3H), 7.18-7.22 (m, 4H), 7.24-7.29 (m, 8H), 7.35-7.39 (m, 3H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 121.5, 127.7, 128.4 (d, J = 7.6 Hz), 128.6, 128.8, 129.9 (d, J = 4.8 Hz), 130.7, 131.3 (d, J = 3.8 Hz), 133.9 (d, J = 20.1 Hz), 134.1, 135.8 (d, J = 14.4 Hz), 137.1 (d, J = 11.5 Hz), 140.5 (d, J = 6.6 Hz), 146.8 (d, J = 27.8 Hz). ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.2. IR (ATR): 3058 w, 1590 w, 1475 w, 1456 w, 1432 m, 1390 w, 1308 w, 1249 w, 1178 w, 1155 w, 1094 w, 1065 w, 1026 w, 1000 m, 825 m, 742 s, 696 s. MS, *m/z* (relative intensity, %): 418 (M$^+$+2, 38), 417 (M$^+$+1, 99), 416 (M$^+$, 39), 415

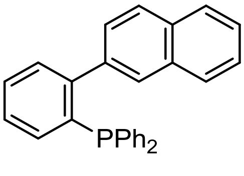
(M^+-1, 100), 337 (10), 259 (12), 257 (17), 183 (15), 169 (16). Exact Mass (CI): Calcd for $C_{24}H_{19}BrP$ 417.0408, found 417.0400.

2-Diphenylphosphino-3'-methylbiphenyl (SM-18)



Method A was followed except that 3-methylphenylboronic acid was used instead of 4-methoxyphenylboronic acid. Colorless oil. Rf 0.40 (hexane/EtOAc = 10/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.19 (s, 3H), 6.90 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.05-7.08 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.17-7.25 (m, 11H), 7.29-7.34 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 21.3, 126.6 (d, *J* = 3.8 Hz), 127.1, 127.4, 127.8, 128.26 (d, *J* = 8.6 Hz), 128.29, 128.5, 129.9 (d, *J* = 4.8 Hz), 130.5 (d, *J* = 3.8 Hz), 133.8 (d, *J* = 19.1 Hz), 134.0, 135.8 (d, *J* = 13.4 Hz), 136.9, 137.8 (d, *J* = 12.5 Hz), 141.5 (d, *J* = 6.6 Hz), 148.3 (d, *J* = 28.7 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -13.1. IR (ATR): 1605 w, 1584 w, 1477 w, 1458 w, 1433 m, 1306 w, 1182 w, 1160 w, 1124 w, 1092 w, 1027 w, 999 w, 907 w, 789 w, 759 m, 742 s, 696 s. MS, *m/z* (relative intensity, %): 352 (M^+, 36), 351 (M^+-1, 100). Exact Mass (EI, 17 eV): Calcd for $C_{25}H_{21}P$ 352.1381, found 352.1373.

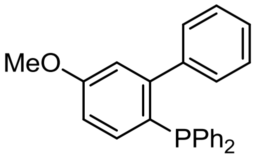
(2-(Naphthalen-2-yl)phenyl)diphenylphosphine (SM-20)



Method A was followed except that 2-naphthylboronic acid was used instead of 4-methoxyboronic acid. White solid. Mp = 149 °C. Rf 0.37 (hexane/EtOAc = 10/1). ^{1}H NMR

(CDCl$_3$, 399.78 MHz) δ: 7.12 (dd, *J* = 7.4, 3.4 Hz, 1H), 7.19-7.29 (m, 11H), 7.36-7.44 (m, 5H), 7.52 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 125.9 (d, *J* = 11.5 Hz), 127.1, 127.4, 127.6, 127.9 (d, *J* = 2.9 Hz), 128.1, 128.3, 128.38, 128.43, 128.7, 128.8 (d, *J* = 3.8 Hz), 130.3 (d, *J* = 4.7 Hz), 132.5 (d, *J* = 26.8 Hz), 133.8, 134.0, 134.2, 136.1 (d, *J* = 14.4 Hz), 137.6 (d, *J* = 12.5 Hz), 139.1 (d, *J* = 6.7 Hz), 148.1 (d, *J* = 28.8 Hz). ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -13.3. IR (ATR): 1475 w, 1454 w, 1434 m, 1157 w, 1128 w, 1092 w, 109 w, 1025 w, 999 w, 944 w, 894 w, 858 m, 821 m, 772 w, 749 s, 739 s, 693 s. MS, *m/z* (relative intensity, %): 389 (M$^+$+1, 11), 388 (M$^+$, 53), 387 (M$^+$-1, 100), 233 (17). Exact Mass (EI, 18 eV): Calcd for $C_{28}H_{21}P$ 388.1381, found 388.1379.

2-Diphenylphosphino-5-methoxybiphenyl (SM-24)

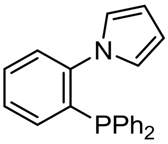


A dry three-necked flask was charged with 2-bromo-5-methoxy-1,1'-biphenyl (1.3 g, 4.9 mmol)[14] and dry Et$_2$O (10 mL) under a nitrogen atmosphere. *n*-BuLi (3.3 mL, 1.6 M in *n*-hexane, 5.4 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min. A solution of ClPPh$_2$ (1.6 g, 7.3 mmol) in Et$_2$O (8 mL) was then added dropwise, and the reaction mixture was stirred overnight. The mixture was filtered through a Celite pad, and the filtrate was evaporated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 10/1) to give a titled compound as a white solid (0.91 g, 51%).

White solid. Mp = 138 °C. Rf 0.34 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.81 (s, 3H), 6.82 (dd, *J* = 11.2, 2.8 Hz, 1H), 6.89 (dd, J = 6.4, 2.8 Hz, 1H), 7.00 (dd, *J* = 12.4, 3.4 Hz, 1H), 7.19-7.23 (m, 6H), 7.27-7.29 (m, 9H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ:

55.2, 113.5, 115.3 (d, *J* = 5.7 Hz), 126.4 (d, *J* = 10.6 Hz), 127.3, 127.5, 128.25 (d, *J* = 9.6 Hz), 128.30, 129.5 (d, *J* = 3.8 Hz), 133.6 (d, *J* = 20.1 Hz), 136.0, 138.3 (d, *J* = 11.5 Hz), 141.7 (d, *J* = 5.8 Hz), 150.0 (d, *J* = 3.7 Hz), 159.8. ^{1}P NMR (CDCl$_3$, 161.8 MHz) δ: -15.4. IR (ATR): 3052 w, 2949 w, 2928 w, 1588 m, 1556 w, 1472 m, 1433 m, 1393 w, 1316 m, 1220 m, 1180 w, 1088 m, 1072 w, 1023 m, 999 w, 911 w, 864 w, 816 w, 766 w, 747 s, 698 s. MS, *m/z* (relative intensity, %): 368 (M$^+$, 42), 367 (M$^+$-1, 100), 145 (10). Exact Mass (EI): Calcd for $C_{25}H_{21}OP$ 368.1330, found 368.1320.

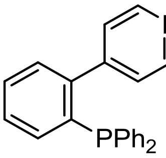
1-(2-(Diphenylphosphino)phenyl)-1*H*-pyrrole (SM-26)



To a three-necked flask containing Mg (0.26 g, 11 mmol) and Et$_2$O (20 mL), 1-(2-bromophenyl)-1*H*-pyrrole [CAS: 69907-27-3][15] (2.2 g, 9.9 mmol) in Et$_2$O (5 mL) was added dropwise under an atmosphere of nitrogen. The reaction mixture was then refluxed for 3 h. After cooling the mixture to room temperature, ClPPh$_2$ (3.3 g, 15 mmol) in Et$_2$O (8 mL) was added dropwise, and the reaction mixture was stirred overnight. A saturated aqueous solution of NH$_4$Cl (20 mL) was added, and the organic phase collected. The aqueous phase was extracted with ether (3×30 mL), and the combined organic extracts were dried over MgSO$_4$. Filtration followed by removal of solvents under reduced pressure afforded the crude product. The crude product was further purified by silica gel column chromatography (hexane/EtOAc = 10:1) to give a desired product as a pale yellow oil (1.5 g, 46%).

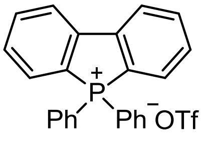
Colorless oil. Rf 0.43 (hexane/EtOAc = 10/1). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 6.30-6.31 (m, 2H), 6.76-6.78 (m, 2H), 7.14-7.16 (m, 1H), 7.32-7.50 (m, 13H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 108.7, 122.8 (d, *J* = 2.9 Hz), 126.8 (d, *J* = 1.9 Hz), 127.5, 128.4 (d, *J* = 6.6 Hz), 128.6, 129.5, 133.7 (d, *J* = 20.1 Hz), 134.5 (d, *J* = 18.2 Hz), 134.7, 136.8 (d, *J* = 11.5 Hz), 145.5 (d, *J* = 23.0 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -16.6. IR (ATR): 1586 w, 1489 w, 1435 w, 1326 w, 1076 w, 1015 w, 905 s, 766 w, 723 s, 696 s. MS, *m/z* (relative intensity, %): 328 (M^{+}+1, 14), 327 (M^{+}, 68), 326 (M^{+}-1, 100), 250 (11), 248 (16), 172 (27), 115 (11). Exact Mass (EI): Calcd for $C_{22}H_{18}NP$ 327.1177, found 327.1173.

4-(2-(Diphenylphosphino)phenyl)pyridine (SM-27)



Method B was followed except that 4-pyridylboronic acid was used instead of 4-cyanophenylboronic acid. White solid. Mp = 108 °C. Rf 0.14 (hexane/EtOAc = 5/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.07 (dd, *J* = 7.6, 3.2 Hz, 1H), 7.11 (d, *J* = 5.6 Hz, 2H), 7.20 (td, *J* = 7.6, 1.9 Hz, 4H), 7.25-7.34 (m, 8H), 7.41 (td, *J* = 7.5, 1.2 Hz, 1H), 8.47 (d, *J* = 6. Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 124.6 (d, *J* = 3.8 Hz), 128.3, 128.5 (d, *J* = 6.7 Hz), 128.7, 128.9, 129.6 (d, *J* = 4.8 Hz), 133.8, 134.0, 135.8 (d, *J* = 16.3 Hz), 136.6 (d, *J* = 11.6 Hz), 145.1 (d, *J* = 26.8 Hz), 149.0, 149.3 (d, *J* = 5.7 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: -12.8. IR (ATR): 1596 w, 1580 w, 1539 w, 1476 w, 1455 w, 1432 m, 1413 w, 1327 w, 1309 w, 1293 w, 1225 w, 1180 w, 1158 w, 1091 w, 1068 w, 1027 w, 992 w, 878 w, 822 m, 741 s, 692 s, 672 m. MS, *m/z* (relative intensity, %): 339 (M^{+}, 42), 338 (M^{+}-1, 100). Exact Mass (EI, 18 eV): Calcd for $C_{23}H_{18}NP$ 339.1177, found 339.1167.

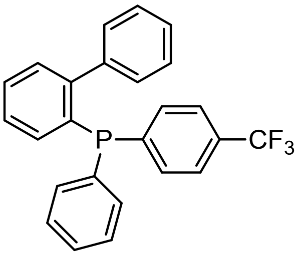
5,5-Diphenyl-5*H*-benzophosphol-5-ium trifluoromethanesulfonate (32)



32 was prepared according to the literature procedure.[16] To a solution of 5-phenyl-5*H*-dibenzophosphole (0.52 g, 2.0 mmol) in acetonitrile (20 mL), CsF (1.8 g, 12 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.5 g, 5.0 mmol) were added successively. After 15 hours of stirring at room temperature, the reaction mixture was quenched with water (2 mL) and was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried on $MgSO_4$ and filtered. The filtrate was then concentrated in vacuo. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH = 50/1) to afford the desired product as a white solid (0.27 g, 27%).

White solid. Mp = 57 °C. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.68-7.76 (m, 6H), 7.81-7.87 (m, 6H), 7.91 (t, J = 7.8 Hz, 2H), 8.12 (dd, J = 10.4, 2.8 Hz, 2H), 8.21 (t, J = 8.6 Hz, 2H) ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 116.1 (d, J = 88.2 Hz), 120.5 (d, J = 87.9 Hz), 123.8 (d, J = 9.6 Hz), 130.8 (d, J = 13.5 Hz), 131.4 (d, J = 12.5 Hz), 132.2 (d, J = 10.6 Hz), 133.1 (d, J = 11.5 Hz), 135.8, 136.7, 143.9 (d, J = 19.2 Hz). ^{1}P NMR ($CDCl_3$, 161.8 MHz) δ: 22.3. IR (ATR): 3061 w, 1590 w, 1474 w, 1442 m, 1257 s, 1224 m, 1149 s, 1109 m, 1080 w, 1028 s, 997 w, 754 m, 723 s, 688 m. Exact Mass (FAB): Calcd for $C_{25}H_{18}P$ [M-OTf]$^+$ 337.1148, found 337.1151.

[1,1'-Biphenyl]-2-yl(phenyl)(4-(trifluoromethyl)phenyl)phosphine (33)



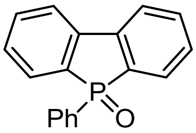
A dry three-necked flask was charged with Cl_2PPh (0.89 g, 5.0 mmol) and dry Et_2O (10 mL) in a nitrogen atmosphere. The solution was cooled to −78 °C. A solution of 2-lithiobiphenyl [prepared from 2-bromobiphenyl (1.2 g, 5.0 mmol) and BuLi (3.4 mL, 1.6 M in *n*-hexane, 5.5 mmol)] in Et_2O (10 mL) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min. A solution of $4\text{-}CF_3C_6H_4MgBr$ [prepared from

1-bromo-4-(trifluoromethyl)benzene (2.3 g, 10 mmol) and Mg (0.27 g, 11 mmol)] in Et_2O (20 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature, and stirred overnight. The reaction mixture was filtered through a Celite pad and evaporated in vacuo. The crude product was purified by silica gel column chromatography (hexane/EtOAc = 10/1) and GPC to give the titled compound as a colorless oil (0.94 g, 46%). Colorless oil. Rf 0.40 (hexane/EtOAc = 10/1). ^1H NMR ($CDCl_3$, 399.78 MHz) δ: 7.04 (dd, J = 7.9, 1.2 Hz, 1H), 7.16-7.18 (m, 2H), 7.21-7.36 (m, 12H), 7.40-7.45 (m, 1H), 7.51 (d, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 124.1 (q, J = 272.1 Hz), 124.9 (q, J = 3.5 Hz), 127.3, 127.5, 127.6, 128.6 (d, J = 7.6 Hz), 129.0 (d, J = 13.4 Hz), 129.6 (d, J = 3.8 Hz), 130.15 (q, J = 32.6 Hz), 130.19 (d, J = 4.8 Hz), 133.6, 133.8 (d, J = 6.7 Hz), 134.0, 134.1, 134.7 (d, J = 13.4 Hz), 136.4 (d, J = 11.5 Hz), 141.4 (d, J = 6.7 Hz), 143.3 (d, J = 15.3 Hz), 148.4 (d, J = 28.8 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: -13.0. IR (ATR): 3055 w, 1605 w, 1461 w, 1433 w, 1394 w, 1322 s, 1165 m, 1123 s, 1107 m, 1060 m, 1015 m, 911 w, 832 m, 773 w, 746 m, 697 s. MS, *m/z* (relative intensity, %): 406 (M^+, 38), 405 (M^+-1, 100), 183 (14). Exact Mass (EI): Calcd for $C_{25}H_{18}F_3P$ 406.1098, found 406.1090.

A representative procedure for the synthesis of phosphole oxides (Table 3.1).

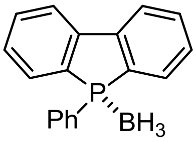
An oven-dried 5 mL screw-capped vial was charged with 2-diphenylphosphinobiphenyl (**1**, 0.10 g, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 160 °C for 12 h followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 0.5 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was purified by flash chromatography (EtOAc) to give 5-phenyl-5*H*-dibenzophosphole 5-oxide (**3**, 67 mg, 80%) as a white solid.

5-Phenyl-5*H*-dibenzophosphole 5-oxide (3) [CAS: 1031-13-6]



White solid. Rf 0.37 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.34-7.40 (m, 4H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.62-7.73 (m, 4H), 7.82 (dd, *J* = 10.4, 2.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 121.1 (d, *J* = 10.7 Hz), 128.6 (d, *J* = 12.5 Hz), 129.3 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 9.6 Hz), 130.6 (d, *J* = 103.4 Hz), 130.9 (d, *J* = 10.5 Hz), 132.1 (d, *J* = 2.8 Hz), 132.7 (d, *J* = 107.3 Hz), 133.3 (d, *J* = 1.9 Hz), 141.6 (d, *J* = 22.1 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.1. MS, *m/z* (relative intensity, %): 277 (M^++1, 12), 276 (M^+, 66), 230 (18), 229 (100), 228 (40), 119 (36), 183 (29), 152 (31). Exact Mass (EI): Calcd for $C_{18}H_{13}OP$ 276.0704, found 276.0701.

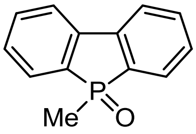
5-Phenyl-5*H*-dibenzophosphole-Borane (4) [CAS: 1354049-96-9]



An oven-dried 5 mL screw-capped vial was charged with 2-diphenylphosphinobiphenyl (**1**, 0.10 mg, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 160 °C for 12 h followed by cooling. To the reaction mixture, BH_3•Me_2S (1 mL) was added under a gentle stream of nitrogen, and the mixture was stirred at room temperature for 12 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with CH_2Cl_2. The filtrate was evaporated, and the residue was purified by flash chromatography (hexane/CH_2Cl_2 = 3/1) to give 5-phenyl-5*H*-dibenzophosphole-borane (**4**, 50 mg, 61%) as a white solid.

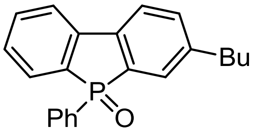
White solid. Rf 0.40 (Hexane/CH_2Cl_2 = 3/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 0.5-1.5 (br, 3H), 7.34 (td, *J* = 7.4, 2.1, 1H), 7.39-7.46 (m, 3H), 7.53-7.62 (m, 4H), 7.71 (t, *J* = 8.0, 2H), 7.93 (d, *J* = 8.0, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 121.7 (d, *J* = 6.7 Hz), 127.8 (d, *J* = 50.8 Hz), 128.9 (d, *J* = 10.5 Hz), 129.1 (d, *J* = 10.6 Hz), 130.5 (d, *J* = 12.5 Hz), 131.7 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 1.9 Hz), 131.1 (d, *J* = 9.7 Hz), 133.5 (d, *J* = 61.3 Hz), 143.3 (d, *J* = 9.6 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 25.2 (br). Exact Mass (FAB): Calcd for $C_{18}H_{13}P$ $[M\text{-}BH_3]^+$ 260.0755, found 260.0753.

5-Methyl-5*H*-benzophosphole 5-oxide (6) [CAS: 19190-40-0]



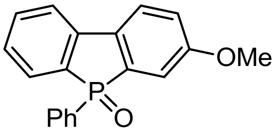
White solid. Mp = 91 °C. Rf 0.14 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 1.85 (d, *J* = 13.2 Hz, 3H), 7.42 (td, *J* = 7.1, 2.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.77 (dd, *J* = 7.8, 2.6 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 16.3 (d, *J* = 71.9 Hz), 121.1 (d, *J* = 9.7 Hz), 128.8 (d, *J* = 9.6 Hz), 129.1 (d, *J* = 11.6 Hz), 132.5 (d, *J* = 105.5 Hz), 133.1, 140.5 (d, *J* = 21.1 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 39.6. MS, *m/z* (relative intensity, %): 214 (M$^+$, 43), 200 (14), 199 (M$^+$-15, 100), 152 (27). IR (ATR): 1597 w, 1471 w, 1440 w, 1411 w, 1291 w, 1268 w, 1192 s, 1178 m, 1128 w, 1083 w, 1067 w, 876 m, 779 w, 758 m, 729 s. Exact Mass (EI): Calcd for $C_{13}H_{11}OP$ 214.0548, found 214.0545.

3-Butyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (7)



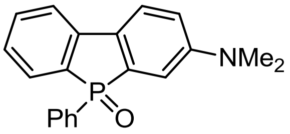
Colorless oil. Rf 0.46 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 0.89 (t, *J* = 7.4 Hz, 3H), 1.32 (sext, *J* = 7.4 Hz, 2H), 1.54-1.61 (m, 2H), 2.58-2.63 (m, 2H), 7.32 (td, *J* = 7.6, 3.5 Hz, 1H), 7.36-7.40 (m, 3H), 7.48 (td, *J* = 7.5, 1.7 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 2H), 7.63-7.72 (m, 4H), 7.77 (dd, *J* = 10.0, 2.8 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 13.8, 22.2, 33.1, 35.3, 120.8 (d, *J* = 9.6 Hz), 120.9 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 12.5 Hz), 128.8 (d, *J* = 11.6 Hz), 129.5 (d, *J* = 9.7 Hz), 129.7 (d, *J* = 10.5 Hz), 130.87 (d, *J* = 103.4 Hz), 130.90 (d, *J* = 11.5 Hz), 132.0 (d, *J* = 2.9 Hz), 132.6 (d, *J* = 107.4 Hz), 132.7 (d, *J* = 104.5 Hz), 133.2, 133.5 (d, *J* = 1.9 Hz), 139.3 (d, *J* = 22.0 Hz), 141.8 (d, *J* = 22.0 Hz), 144.6 (d, *J* = 10.6 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.1. IR (ATR): 2957 w, 2930 w, 2860 w, 1594 w, 1481 w, 1441 w, 1188 m, 1134 w, 1111 w, 1082 w, 1064 w, 907 m, 837 w, 773 w, 725 s, 692 m. MS, *m/z* (relative intensity, %): 333 (M^++1, 16), 332 (M^+, 71), 290 (30), 289 (100), 241 (24), 239 (20), 229 (31), 212 (11). Exact Mass (EI): Calcd for $C_{19}H_{15}OP$ 332.1330, found 332.1331.

3-Methoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide (8) [CAS: 1332483-72-3]



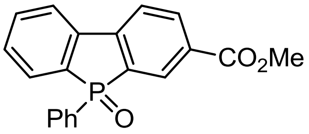
White solid. Rf 0.34 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 3.79 (s, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 11.0, 2.2 Hz, 1H), 7.27-7.31 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.63-7.73 (m, 5H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 55.6, 113.8 (d, *J* = 10.6 Hz), 119.8, 120.4 (d, *J* = 9.6 Hz), 122.4 (d, *J* = 11.5 Hz), 120.2 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 12.5 Hz), 129.7 (d, *J* = 9.6 Hz), 130.7 (d, *J* = 102.5 Hz), 130.9 (d, *J* = 11.5 Hz), 132.1 (d, *J* = 2.8 Hz), 132.2 (d, *J* = 108.3 Hz), 133.4, 134.2 (d, *J* = 22.0 Hz), 134.4 (d, *J* = 106.3 Hz), 141.8 (d, *J* = 22.0 Hz), 160.7 (d, *J* = 14.4 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.0. MS, *m/z* (relative intensity, %): 307 (M^++1, 21), 306 (M^+, 100), 259 (30), 258 (23), 244 (18), 229 (31), 227 (12), 215 (19), 213 (27), 186 (13). Exact Mass (EI): Calcd for $C_{19}H_{15}O_2P$ 306.0810, found 306.0809.

3-(Dimethylamino)-5-phenyl-5*H*-dibenzophosphole 5-oxide (9)



Yellow-green solid. Mp = 114 °C. Rf 0.29 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 2.99 (s, 6H), 6.85 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.01 (dd, *J* = 11.8, 2.6 Hz, 1H), 7.21 (td, *J* = 8.0, 3.6 Hz, 1H), 7.38 (td, *J* = 7.5, 3.1 Hz, 2H), 7.46-7.51 (m, 2H), 7.59-7.69 (m, 5H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 40.4, 112.4 (d, *J* = 12.5 Hz), 116.1 (d, *J* = 2.0 Hz), 119.7 (d, *J* = 10.6 Hz), 122.1 (d, *J* = 11.5 Hz), 127.1 (d, *J* = 11.5 Hz), 128.0 (d, *J* = 12.5 Hz), 128.6 (d, *J* = 12.5 Hz), 129.6 (d, *J* = 9.6 Hz), 131.0 (d, *J* = 10.5 Hz), 131.6 (d, *J* = 102.5 Hz), 131.7 (d, *J* = 108.3 Hz), 131.9 (d, *J* = 1.9 Hz), 133.2 (d, *J* = 1.9 Hz), 134.0 (d, *J* = 106.4 Hz), 142.8 (d, *J* = 22.1 Hz), 151.1 (d, *J* = 13.4 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 35.0. IR (ATR): 3054 w, 2923 w, 2809 w, 1589 s, 1559 m, 1501 m, 1454 m, 1437 s, 1360 s, 1297 m, 1193 s, 1130 m, 1110 m, 1060 m, 1027 w, 1000 w, 957 w, 825 m, 768 m, 728 s, 695 m. MS, *m/z* (relative intensity, %): 320 (M+1, 20), 319 (M+, 100), 318 (M+-1,22), 305 (32), 304 (25), 226 (19). Exact Mass (EI): Calcd for $C_{20}H_{18}NOP$ 319.1126, found 319.1123.

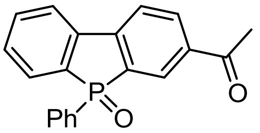
Methyl 5-phenyl-5*H*-benzophospole-3-carboxylate 5-oxide (10)



White solid. Mp = 167 °C. Rf 0.34 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.90 (s, 3H), 7.38-7.53 (m, 4H), 7.62-7.67 (m, 3H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.90 (dd, *J* = 8.2, 2.6 Hz, 2H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.37 (dd, *J* = 10.0, 1.2 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 52.3, 121.1 (d, *J* = 10.5 Hz), 122.0 (d, *J* = 9.6 Hz), 128.77 (d, *J* = 12.5 Hz), 128.83 (d, *J* = 97.7 Hz), 130.0 (d, *J* = 9.7 Hz), 130.4 (d, *J* = 11.5 Hz), 131.0 (d, *J* = 10.6 Hz), 131.1 (d, *J* = 10.6 Hz), 132.0 (d, *J* = 9.6 Hz), 132.4 (d, *J* = 2.8 Hz), 133.3 (d, *J* = 107.4 Hz), 133.55, 133.57

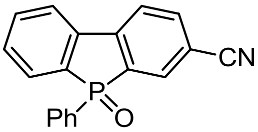
(d, J = 107.3 Hz), 134.8, 140.6 (d, J = 21.0 Hz), 145.6 (d, J = 22.0 Hz), 165.7. ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.0. IR (ATR): 2947 w, 1712 s, 1602 m, 1479 w, 1460 w, 1433 m, 1406 w, 1332 w, 1281 m, 1255 s, 1225 m, 1195 s, 1145 m, 1119 s, 1107 s, 998 w, 972 w, 919 w, 852 m, 793 w, 757 s, 726 s, 692 s. MS, *m/z* (relative intensity, %): 335 (M^++1, 21), 334 (M^+, 100), 303 (16), 287 (34), 275 (14), 257 (49), 255 (34), 244 (15), 243 (58), 241 (47), 229 (15), 228 (80), 227 (27), 226 (27), 199 (10), 198 (14), 51 (17). Exact Mass (EI): Calcd for $C_{20}H_{15}O_3P$ 334.0759, found 334.0757.

3-Acetyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (11)



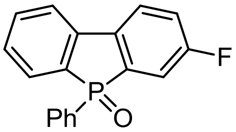
White solid. Mp = 201 °C. Rf 0.31 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.58 (s, 3H), 7.39-7.48 (m, 3H), 7.52 (td, J = 7.3, 1.3 Hz, 1H), 7.62-7.68 (m, 3H), 7.75 (t, J = 8.4 Hz, 1H), 7.91 (td, J = 8.0, 2.8 Hz, 2H), 8.20 (d, J = 8.0 Hz, 1H), 8.26 (dd, J = 10.0, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 26.7, 121.3 (d, J = 9.6 Hz), 122.1 (d, J = 10.6 Hz), 128.8 (d, J = 12.5 Hz), 129.75 (d, J = 104.5 Hz), 129.83(d, J = 9.6 Hz), 130.0 (d, J = 9.6 Hz), 130.5 (d, J = 11.5 Hz), 131.0 (d, J = 10.6 Hz), 132.4 (d, J = 2.8 Hz), 133.2, 133.4, 133.5 (d, J = 106.4 Hz), 133.8 (d, J = 107.4 Hz), 137.6 (d, J = 9.6 Hz), 140.5 (d, J = 21.1 Hz), 145.7 (d, J = 22.0 Hz), 196.4. ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.0. IR (ATR): 1677 m, 1595 m, 1475 w, 1438 w, 1409 w, 1352 w, 1275 w, 1248 m, 1200 s, 1159 m, 1131 w, 1109 m, 1089 m, 1020 w, 966 w, 914 w, 901 w, 839 w, 821 w, 788 m, 756 m, 731 s, 692 s, 663 w. MS, *m/z* (relative intensity, %): 319 (M^++1, 17), 318 (M^+, 87), 304 (22), 303 (M^+-15, 100), 275 (42), 254 (11), 241 (13), 228 (13), 226 (18), 225 (13), 198 (15), 51 (10). Exact Mass (EI): Calcd for $C_{20}H_{15}O_2P$ 318.0810, found 318.0813.

3-Cyano-5-phenyl-5*H*-dibenzophosphole 5-oxide (12)



White solid. Mp = 240 °C. Rf 0.40 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.43 (td, *J* = 7.4, 3.1 Hz, 2H), 7.48-7.57 (m, 2H), 7.60-7.70 (m, 3H), 7.77 (t, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.92-7.96 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 113.0 (d, *J* = 13.4 Hz), 117.8, 121.8 (d, *J* = 9.6 Hz), 122.2 (d, *J* = 10.6 Hz), 128.98 (d, *J* = 12.5 Hz), 129.02 (d, *J* = 105.5 Hz), 130.3 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 10.5 Hz), 131.1 (d, *J* = 11.6 Hz), 132.8 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 107.4 Hz), 133.3 (d, *J* = 10.6 Hz), 133.9 (d, *J* = 1.9 Hz), 134.6 (d, *J* = 104.5 Hz), 136.9, 139.9 (d, *J* = 20.2 Hz), 145.4 (d, *J* = 21.1 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 32.7. IR (ATR): 2231 w, 1596 w, 1473 w, 1435 m, 1403 w, 1290 w, 1227 m, 1212 m, 1191 m, 1174 m, 1135 m, 1106 m, 1080 w, 1065 w, 1024 w, 924 w, 862 w, 837 m, 765 m, 728 s, 698 s, 665 w. MS, *m/z* (relative intensity, %): 301 (M^+, 42), 255 (23), 254 (100), 253 (22), 224 (24), 208 (23), 177 (19), 51 (12). Exact Mass (EI): Calcd for $C_{19}H_{12}NOP$ 301.0657, found 301.0658.

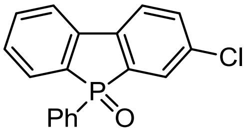
3-Fluoro-5-phenyl-5*H*-dibenzophosphole 5-oxide (13)



White solid. Mp = 178 °C. Rf 0.46 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.25 (td, *J* = 8.5, 1.9 Hz, 1H), 7.35-7.43 (m, 4H), 7.49-7.54 (m, 1H), 7.56-7.72 (m, 4H), 7.76-7.81 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 116.8 (dd, *J* = 33.6, 10.6 Hz), 120.4 (d, *J* = 22.9, 1.9 Hz), 120.9 (d, *J* = 10.6 Hz), 122.9 (dd, *J* = 12.4, 7.7 Hz), 128.8 (d, *J* = 13.5 Hz), 129.1 (d, *J* = 10.6 Hz), 129.97 (d, *J* = 10.6 Hz), 130.00 (d, *J* = 103.4 Hz), 130.9 (d, *J* = 11.5 Hz), 132.4 (d, *J* = 1.9 Hz), 132.5 (d, *J* = 108.3 Hz), 133.6 (d, *J* = 1.9 Hz), 135.4 (dd, *J* = 105.4, 6.7 Hz), 137.6

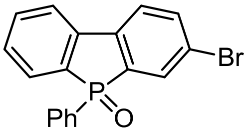
(dd, *J* = 21.1, 2.9 Hz), 141.0 (d, *J* = 21.1 Hz), 163.3 (dd, *J* = 252.0, 15.3 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.1. IR (ATR): 1591 w, 1479 m, 1437 s, 1259 m, 1231 w, 1196 s, 1157 m, 1134 m, 1124 m, 1106 m, 1071 w, 1053 w, 1022 w, 999 w, 899 w, 869 w, 829 m, 764 m, 742 s, 727 s, 696 s, 675 m. MS, *m/z* (relative intensity, %): 295 (M^++1, 21), 294 (M^+, 100), 291 (M^+-1, 11), 248 (17), 247 (91), 246 (56), 244 (14), 227 (35), 226 (14), 217 (50), 201 (42), 170 (39), 51 (13). Exact Mass (EI): Calcd for $C_{18}H_{12}FOP$ 294.0610, found 294.0608.

3-Chloro-5-phenyl-5*H*-dibenzophosphole 5-oxide (14) [CAS: 1332483-74-5]



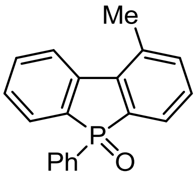
White solid. Rf 0.46 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.37-7.43 (m, 3H), 7.50-7.53 (m, 2H), 7.57-7.75 (m, 6H), 7.78 (dd, *J* = 8.0, 3.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 121.2 (d, *J* = 9.6 Hz), 122.4 (d, *J* = 11.6 Hz), 128.8 (d, *J* = 12.5 Hz), 129.6 (d, *J* = 11.6 Hz), 129.7 (d, *J* = 10.6 Hz), 129.85 (d, *J* = 104.5 Hz), 129.94 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 10.6 Hz), 132.39 (d, *J* = 108.3 Hz), 132.41 (d, *J* = 2.9 Hz), 133.3, 133.6 (d, *J* = 1.9 Hz), 134.9 (d, *J* = 90.1 Hz), 135.5, 139.9 (d, *J* = 21.1 Hz), 140.8 (d, *J* = 21.1 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.2. MS, *m/z* (relative intensity, %): 312 (M^++2, 34), 311 (M^++1, 22), 310 (M^+, 100), 275 (16), 274 (20), 265 (16), 264 (20), 263 (49), 262 (37), 235 (15), 233 (46), 229 (16), 228 (85), 227 (17), 226 (27), 219 (13), 217 (41), 186 (29), 151 (17), 150 (10), 51 (18). Exact Mass (EI): Calcd for $C_{18}H_{12}ClOP$ 310.0314, found 310.0312.

3-Bromo-5-phenyl-5*H*-dibenzophosphole 5-oxide (15)



White solid. Mp = 187 °C. Rf 0.43 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.41 (td, *J* = 7.5, 2.8 Hz, 3H), 7.52 (td, *J* = 7.5, 1.6 Hz, 1H), 7.58-7.72 (m, 6H), 7.78-7.81 (m, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 121.2 (d, *J* = 9.6 Hz), 122.7 (d, *J* = 10.6 Hz), 123.5 (d, *J* = 14.4 Hz), 128.8 (d, *J* = 12.5 Hz), 129.7 (d, *J* = 11.5 Hz), 129.9 (d, *J* = 104.5 Hz), 130.0 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 11.5 Hz), 132.3 (d, *J* = 107.3 Hz), 132.4 (d, *J* = 2.8 Hz), 132.6 (d, *J* = 10.6 Hz), 133.6 (d, *J* = 1.9 Hz), 135.3 (d, *J* = 104.5 Hz), 136.2 (d, *J* = 1.9 Hz), 140.4 (d, *J* = 21.1 Hz), 140.8 (d, *J* = 21.1 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 33.2. IR (ATR): 1591 w, 1469 w, 1433 m, 1394 w, 1224 w, 1201 s, 1160 w, 1135 m, 1107 m, 1084 m, 886 w, 826 m, 794 m, 766 m, 725 s, 696 s. MS, *m/z* (relative intensity, %): 355 (M$^+$+2, 41), 352 (M$^+$, 41), 279 (18), 277 (18), 275 (27), 263 (15), 261 (15), 229 (21), 228 (100), 226 (15), 51 (10). Exact Mass (EI): Calcd for $C_{18}H_{12}BrOP$ 353.9809, found 353.9805.

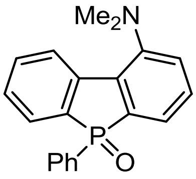
1-Methyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (16)



White sold. Mp = 176 °C. Rf 0.34 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 2.77 (s, 3H), 7.28 (td, *J* = 7.3, 3.8 Hz, 1H), 7.36-7.39 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.57-7.66 (m, 4H), 7.75 (dd, *J* = 10.6, 7.4 Hz, 1H), 8.03 (dd, *J* = 8.0, 3.6 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 22.9, 125.3 (d, *J* = 10.6 Hz), 127.7 (d, *J* = 9.7 Hz), 128.57 (d, *J* = 11.5 Hz), 128.63 (d, *J* = 13.5 Hz), 129.0 (d, *J* = 11.5 Hz), 130.1 (d, *J* = 9.6 Hz), 130.95 (d, *J* = 105.5 Hz), 131.04 (d, *J* = 10.5 Hz), 132.0 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 1.9 Hz), 133.5 (d, *J* = 105.4 Hz), 133.7 (d, *J* = 105.5 Hz), 134.9 (d, *J* = 10.6 Hz), 136.8 (d, *J* = 1.9 Hz), 139.7 (d, *J* = 22.0 Hz), 143.2 (d, *J* = 21.0 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 33.0. IR (ATR): 3060 w, 190 w, 1562 w, 1470 w, 1442 m, 1385 w, 1284 w, 1201 s, 1177 m, 1136 m, 1109 m, 1069 w, 875 w, 779 m, 759 m, 720 s, 695 s, 660 m. MS, *m/z* (relative intensity, %): 291 (M$^+$+1, 17), 290 (M$^+$, 100), 289

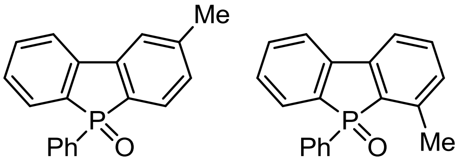
(M^+-1, 13), 244 (15), 243 (91), 242 (20), 241 (18), 228 (38), 213 (42), 197 (46), 166 (16), 165 (38), 135 (12), 51 (25). Exact Mass (EI): Calcd for $C_{19}H_{15}OP$ 290.0861, found 290.0858.

1-Dimethylamino-5-phenyl-5*H*-dibenzophosphole 5-oxide (17)



Yellow-green solid. Mp = 46 °C. Rf 0.37 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.81 (s, 3H), 2.83 (s, 3H), 7.29-7.40 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.61-7.71 (m, 3H), 8.55 (dd, *J* = 8.4, 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 44.3, 44.7, 124.0 (d, *J* = 9.7 Hz), 124.2, 125.9 (d, *J* = 9.6 Hz), 128.3 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 12.4 Hz), 129.4 (d, *J* = 9.6 Hz), 130.0 (d, *J* = 13.4 Hz), 130.95 (d, *J* = 103.4 Hz), 131.00 (d, *J* = 10.6 Hz), 132.0, 133.3, 133.5 (d, *J* = 101.5 Hz), 133.8, 134.9 (d, *J* = 105.4 Hz), 142.0 (d, *J* = 22.0 Hz), 151.7 (d, *J* = 12.5 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.3. IR (ATR): 3058 w, 2943 w, 2866 w, 2833 w, 2787 w, 1580 w, 1479 w, 1451 m, 1438 m, 1314 w, 1285 w, 1195 s, 1157 m, 1133 m, 1110 m, 1068 w, 963 w, 925 w, 826 w, 802 w, 752 m, 724 s, 694 m. MS, *m/z* (relative intensity, %): 320 (M^++1, 22), 319 (M^+, 100), 318 (M^+-1, 39), 302 (13), 240 (11), 226 (16), 224 (10). Exact Mass (EI): Calcd for $C_{20}H_{18}NOP$ 319.1126, found 319.1122.

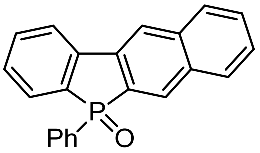
2-Methyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (18) [1332483-75-6]

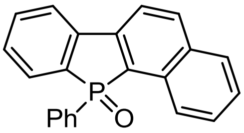


The reaction of **SM-18** gave an inseparable mixture of **18** and **19** in a ratio of 10:1. The spectroscopic data for **18** is as follows. White solid. Rf 0.37 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 2.40 (s, **19**), 2.47 (s, 3H, **18**), 7.20 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.38 (td, *J* = 8.0, 3.2 Hz, 3H), 7.46-7.51 (m, 1H), 7.56-7.73 (m, 6H), 7.81 (dd, *J* = 8.0, 3.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 21.9, 120.9 (d, *J* = 10.6 Hz), 121.8 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 12.5 Hz), 129.5 (d, *J* = 109.3 Hz), 129.6 (d, *J* = 5.7 Hz), 129.7 (d, *J* = 5.8 Hz), 130.2 (d, *J* = 11.5 Hz), 130.9 (d, *J* = 10.6 Hz), 131.0 (d, *J* = 103.5 Hz), 131.9 (d, *J* = 2.9 Hz), 133.1 (d, *J* = 1.9 Hz), 133.2 (d, *J* = 107.3 Hz), 141.7 (d, *J* = 22.0 Hz), 142.0 (d, *J* = 22.0 Hz), 144.0 (d, *J* = 1.9 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.8. IR (ATR): 3043 w, 2922 w, 1604 w, 1591 w, 1469 w, 1436 m, 1201 s, 1183 s, 1134 m, 1113 m, 1091 m, 1066 w, 997 w, 957 w, 924 w, 871 w, 819 w, 773 m, 750 m, 730 s, 695 s. MS, *m/z* (relative intensity, %): 291 (M^++1, 11), 290 (M^+, 94), 244 (20), 243 (100), 242 (35), 241 (13), 228 (38), 213 (59), 197 (46), 166 (16), 165 (34), 51 (11). Exact Mass (EI): Calcd for $C_{19}H_{15}OP$ 290.0861, found 290.0857.

The formation of **19** was confirmed by GCMS and ^{31}P NMR analysis, in which **18** and **19** had different retention times. MS, *m/z* (relative intensity, %): 291 (M^++1, 19), 290 (M^++1, 100), 289 (M^+-1, 58), 243 (36), 242 (13), 241 (15), 228 (22), 213 (15), 207 (16), 183 (18), 165 (17), 78 (16), 73 (13), 51 (12). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.3.

5-Phenyl-5*H*-dibenzo[*b*, *f*]phosphole 5-oxide (20) [1332483-78-9] and 11-phenyl-11*H*-dibenzo[*b*,*g*]phosphole 11-oxide (21)

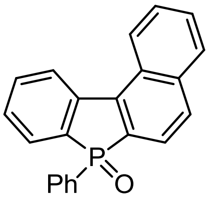




The reaction of **SM-20** gave a mixture of **20** and **21** in a ratio of 2.8:1. The major isomer **20** could be purified by GPC. Spectroscopic data for **20** were as follows: White solid. Rf 0.43 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.36-7.43 (m, 3H), 7.47-7.51 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.62-7.70 (m, 3H), 7.75 (t, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 8.00 (dd, *J* = 7.6, 2.8 Hz, 1H), 8.22-8.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 120.0 (d, *J* = 9.6 Hz), 121.5 (d, *J* = 10.5 Hz), 127.1, 128.55, 128.61, 128.7, 129.2, 129.5 (d, *J* = 10.6 Hz), 129.9 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 107.3 Hz), 131.1 (d, *J* = 11.6 Hz), 131.4 (d, *J* = 104.5 Hz), 131.8 (d, *J* = 9.6 Hz), 132.1 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 106.4 Hz), 133.48 (d, *J* = 6.6 Hz), 133.53 (d, *J* = 7.7 Hz), 135.8, 137.3 (d, *J* = 22.0 Hz), 142.1 (d, *J* = 20.1 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.0. MS, *m/z* (relative intensity, %): 327 (M^++1, 23), 326 (M^+, 100), 279 (45), 278 (56), 250 (14), 249 (63), 233 (39), 202 (26). Exact Mass (EI): Calcd for $C_{22}H_{15}OP$ 326.0861, found 326.0858.

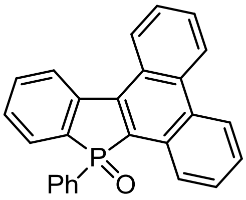
The formation of **21** was confirmed by ^{1}H and ^{31}P NMR and GCMS. ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.34-7.42 (m, 3H), 7.44-7.50 (m, 3H), 7.54 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.64-7.76 (m, 2H), 7.86-7.90 (m, 2H), 7.94 (dd, *J* = 8.6, 2.6 Hz, 1H), 8.10 (d, *J* = 7.2 Hz, 2H). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.7. MS, *m/z* (relative intensity, %): 327 (M^++1, 22), 326 (M^+, 100), 325 (M^+-1, 86), 279 (20), 278 (33), 277 (14), 276 (14), 249 (26), 202 (29).

7-Phenyl-7*H*-dibenzo[*b*, *e*]phosphole 7-oxide (22)



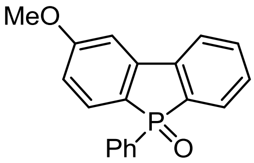
White solid. Mp = 120 °C. Rf 0.37 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.37 (td, *J* = 7.6, 2.8 Hz, 2H), 7.43 (dd, *J* = 7.2, 3.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.62-7.70 (m, 5H), 7.74 (t, *J* = 8.8 Hz, 1H), 7.80 (dd, *J* = 10.4, 7.2 Hz, 1H), 7.88 (dd, *J* = 8.4, 3.2 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.51 (dd, *J* = 8.2, 3.4 Hz, 1H), 8.85 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 124.2 (d, *J* = 10.6 Hz), 124.7, 125.5 (d, *J* = 10.6 Hz), 127.8 (d, *J* = 19.2 Hz), 128.5 (d, *J* = 11.5 Hz), 128.75 (d, *J* = 12.4 Hz), 128.81 (d, *J* = 11.6 Hz), 129.8, 130.3 (d, *J* = 9.6 Hz), 130.7 (d, *J* = 10.6 Hz), 131.2 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 113.1 Hz), 132.1 (d, *J* = 10.6 Hz), 132.17 (d, *J* = 104.5 Hz), 131.20 (d, *J* = 2.0 Hz), 133.3, 134.1 (d, *J* = 105.4 Hz), 137.0, 139.0 (d, *J* = 21.1 Hz), 143.1 (d, *J* = 23.0 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.0. IR (ATR): 3056 w, 1586 w, 1550 w, 1510 w, 1483 w, 1453 m, 1438 m, 1356 w, 1335 w, 1309 w, 1196 s, 1135 m, 1116 m, 1068 w, 1026 w, 998 w, 875 w, 817 m, 795 w, 750 m, 725 s, 694 s, 666 m. MS, *m/z* (relative intensity, %): 327 (M^++1, 12), 326 (M^+, 100), 325 (M^+-1, 12), 279 (52), 278 (61), 277 (23), 276 (16), 249 (30), 233 (34), 202 (35). Exact Mass (EI): Calcd for $C_{22}H_{15}OP$ 326.0861, found 326.0863.

9-Phenyl-9*H*-tribenzo[*b, e, g*]phosphole 9-oxide (23)



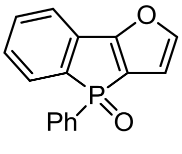
White solid. Mp = 189 °C. Rf 0.49 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.34 (td, *J* = 7.5, 2.9 Hz, 2H), 7.40-7.46 (m, 2H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.60-7.68 (m, 2H), 7.71-7.85 (m, 5H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.51 (dd, *J* = 8.2, 3.8 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 1H), 8.80 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.97 (dd, *J* = 8.0, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 123.0, 124.0, 125.5 (d, *J* = 10.6 Hz), 125.7, 126.9 (d, *J* = 5.7 Hz), 127.3, 127.9 (d, *J* = 19.2 Hz), 128.5, 128.8 (d, *J* = 12.5 Hz), 128.8 (d, *J* = 11.6 Hz), 128.9 (d, *J* = 108.3 Hz), 129.2 (d, *J* = 9.6 Hz), 130.0 (d, *J* = 10.6 Hz), 130.5, 130.6 (d, *J* = 15.3 Hz), 130.7 (d, *J* = 101.5 Hz), 131.0 (d, *J* = 10.6 Hz), 132.0 (d, *J* = 14.4 Hz), 132.1, 133.0, 133.8, 134.5 (d, *J* = 106.4 Hz), 139.4 (d, *J* = 20.1 Hz), 142.4 (d, *J* = 23.0 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.3. IR (ATR): 1587 w, 1450 w, 1436 w, 1366 w, 1192 m, 1139 w, 1110 m, 1068 w, 993 w, 753 s, 721 s, 692 s, 658 m. MS, *m/z* (relative intensity, %): 377 (M^++1, 27), 376 (M^+, 100), 375 (M^+-1, 78), 328 (20), 327 (13), 326 (12), 299 (10), 252 (25), 250 (11). Exact Mass (EI): Calcd for $C_{26}H_{17}OP$ 376.1017, found 376.1014.

2-Methoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide (24)



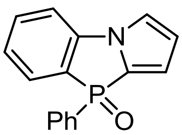
White solid. Mp = 152 °C. Rf 0.29 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.90 (s, 3H), 6.88 (dt, *J* = 8.4, 2.6 Hz, 1H), 7.32 (t, *J* = 2.0 Hz, 1H), 7.37 (td, *J* = 7.5, 3.3 Hz, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.60-7.70 (m, 4H), 7.77 (dd, *J* = 7.8, 2.6 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 55.5, 107.1 (d, *J* = 10.6 Hz), 114.6 (d, *J* = 12.5 Hz), 121.0 (d, *J* = 9.7 Hz), 123.8 (d, *J* = 113.1 Hz), 128.5 (d, *J* = 12.5 Hz), 129.5 (d, *J* = 7.6 Hz), 129.6 (d, *J* = 6.7 Hz), 130.9 (d, *J* = 10.6 Hz), 131.30 (d, *J* = 11.5 Hz), 131.31 (d, *J* = 136.0 Hz), 131.9, 133.1, 133.9 (d, *J* = 106.4 Hz), 141.2 (d, *J* = 22.0 Hz), 144.1 (d, *J* = 22.9 Hz), 164.0. ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 32.9. IR (ATR): 1596 m, 1569 m, 1483 m, 1437 m, 1315 m, 1238 m, 1184 s, 1134 m, 1110 m, 1090 m, 1065 m, 1024 m, 876 m, 824 m, 774 m, 751 m, 730 s, 694 s. MS, *m/z* (relative intensity, %): 307 (M$^+$+1, 22), 306 (M$^+$, 100), 260 (13), 259 (66), 258 (35), 244 (26), 230 (11), 229 (75), 228 (11), 227 (14), 215 (24), 214 (16), 213 (64), 186 (27), 157 (19), 51 (15). Exact Mass (EI): Calcd for $C_{19}H_{15}O_2P$ 306.0810, found 306.0809.

4-Phenyl-4*H*-phospholo[3,2-*b*]furan 4-oxide (25)



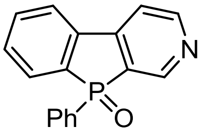
Pale purple oil. Rf 0.37 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 6.60 (t, *J* = 1.8 Hz, 1H), 7.29 (tq, *J* = 7.2, 1.4 Hz, 1H), 7.42 (td, *J* = 7.6, 3.2 Hz, 2H), 7.46-7.52 (m, 3H), 7.55 (q, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 10.8, 7.2 Hz, 1H), 7.71-7.76 (m, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 110.3 (d, *J* = 8.5 Hz), 116.3 (d, *J* = 123.7 Hz), 118.7 (d, *J* = 8.6 Hz), 128.7 (d, *J* = 12.5 Hz), 128.9 (d, *J* = 11.5 Hz), 129.7 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 109.3 Hz), 130.9 (d, *J* = 10.6 Hz), 132.0 (d, *J* = 9.6 Hz), 132.3 (d, *J* = 1.9 Hz), 132.5, 133.0 (d, *J* = 12.5 Hz), 138.2 (d, *J* = 107.3 Hz), 147.2 (d, *J* = 10.6 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 20.9. IR (ATR): 1528 w, 1482 w, 1438 w, 1400 w, 1269 w, 1228 m, 1188 m, 1143 w, 1121 w, 1110 w, 1080 w, 1048 w, 1028 w, 908 m, 893 w, 769 m, 723 s, 688 s. MS, *m/z* (relative intensity, %): 267 (M^++1, 18), 266 (M^+, 100), 219 (15), 218 (24), 191 (17), 190 (11), 189 (66), 173 (12), 133 (17), 114 (12). Exact Mass (EI): Calcd for $C_{16}H_{11}O_2P$ 266.0497, found 266.0499.

9-Phenyl-9*H*-benzo[*d*]pyrrolo[1,2-*a*][1,3]azaphosphole 9-oxide (26)



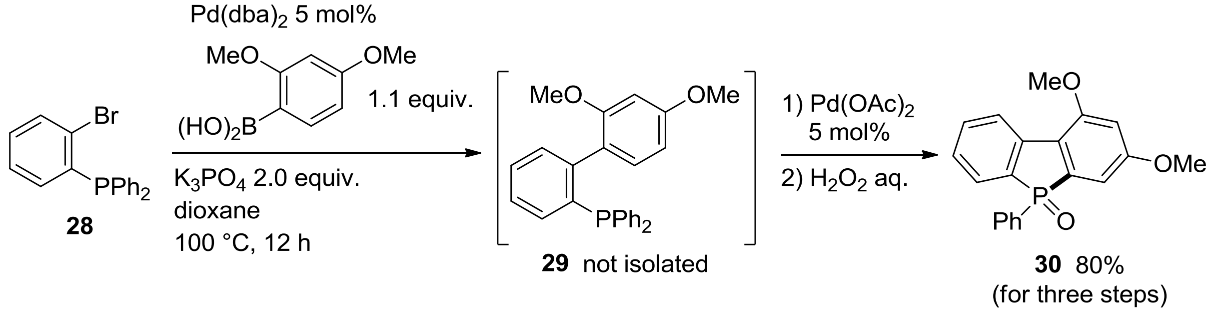
White solid. Mp = 146 °C. Rf 0.37 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 6.46 (q, *J* = 3.1 Hz, 1H), 6.79 (td, *J* = 2.3, 0.93 Hz, 1H), 7.19 (td, *J* = 7.4, 3.3 Hz, 1H), 7.34-7.37 (m, 2H), 7.43 (td, *J* = 7.8, 3.2 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.60 (dd, *J* = 10.6, 7.4 Hz, 1H), 7.71 (dd, *J* = 14.0, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 111.7 (d, *J* = 6.7 Hz), 115.5 (d, *J* = 10.6 Hz), 117.7 (d, *J* = 13.4 Hz), 117.9 (d, *J* = 6.7 Hz), 124.7 (d, *J* = 133.2 Hz), 125.7 (d, *J* = 11.6 Hz), 126.6 (d, *J* = 104.5 Hz), 128.7 (d, *J* = 13.4 Hz), 130.3 (d, *J* = 6.6 Hz), 130.8 (d, *J* = 117.9 Hz), 131.3 (d, *J* = 11.6 Hz), 132.3 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 1.9 Hz), 142.0 (d, *J* = 10.6 Hz). ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 14.8. IR (ATR): 1602 w, 1582 w, 1517 w, 1478 m, 1461 w, 1435 w, 1389 w, 1349 w, 1331 w, 1296 w, 1221 w, 1194 m, 1135 w, 1113 m, 1087 w, 1065 w, 1026 w, 962 w, 908 m, 755 m, 723 s, 691 s. MS, *m/z* (relative intensity, %): 266 (M^++1, 19), 265 (M^+, 100), 218 (47), 217 (59), 188 (28), 172 (27), 133 (18), 115 (11), 107 (15), 51 (11). Exact Mass (EI): Calcd for $C_{16}H_{12}NOP$ 265.0657, found 265.0656.

3-Azadibenzophosphole 5-oxide (27) [CAS: 1312012-54-6]



White solid. Rf 0.14 (EtOAc). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 7.43 (td, *J* = 7.7, 3.1 Hz, 2H), 7.52-7.58 (m, 2H), 7.63-7.70 (m, 3H), 7.72-7.73 (m, 1H), 7.79 (t, *J* = 8.6 Hz, 1H), 7.92 (dd, *J* = 7.8, 2.6 Hz, 1H), 8.81 (dd, *J* = 5.2, 2.4 Hz, 1H), 8.91 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 115.8 (d, *J* = 7.6 Hz), 122.5 (d, *J* = 9.7 Hz), 128.1 (d, *J* = 103.4 Hz), 128.9 (d, *J* = 12.5 Hz), 129.5 (d, *J* = 103.4 Hz), 130.2 (d, *J* = 10.6 Hz), 130.9 (d, *J* = 11.6 Hz), 131.9 (d, *J* = 11.6 Hz), 132.7 (d, *J* = 2.9 Hz), 133.4 (d, *J* = 107.4 Hz), 133.7 (d, *J* = 1.9 Hz), 139.3 (d, *J* = 21.1 Hz), 149.4 (d, *J* = 20.1 Hz), 150.7 (d, *J* = 10.6 Hz), 154.1. ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 33.5. MS, *m/z* (relative intensity, %): 278 (M^++1, 15), 277 (M^+, 100), 276 (M^+-1, 29), 231 (16), 230 (82), 229 (22), 202 (11), 200 (33), 184 (30), 153 (15), 126 (20), 51 (14). Exact Mass (EI): Calcd for $C_{17}H_{12}NOP$ 277.0657, found 277.0657.

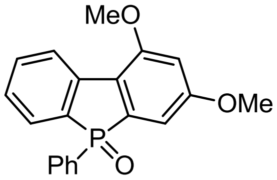
A Procedure for Scheme 3.3



A two-necked flask was charged with **28** (0.10 g, 0.30 mmol), 2,4-dimethoxyphenylboronic acid (60 mg, 0.33 mmol), $Pd(dba)_2$ (8.6 mg, 0.015 mmol), K_3PO_4 (0.13 g, 0.60 mmol) and 1 mL of dioxane under an atmosphere of nitrogen. The mixture was stirred at 100 °C for 12 h and cooled to room temperature. After filtration through a Celite pad, the solvent was evaporated to give crude **29** (0.13 g).

An oven-dried 5 mL screw-capped vial was charged with crude **29** (0.13 g), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 160 °C for 12 h, followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 0.5 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was subjected to flash chromatography (EtOAc) to give 1,3-dimethoxy-5-phenyl- 5*H*-dibenzophosphole 5-oxide (**30**, 80 mg, 80%) as a white solid.

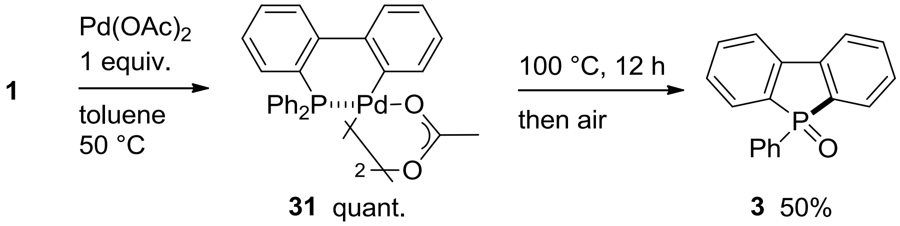
1,3-Dimethoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide (30)



White sold. Mp = 184 °C. Rf 0.31 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 3.79 (s, 3H), 3.98 (s, 3H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.83 (dd, *J* = 11.0, 1.8 Hz, 1H), 7.22-7.27 (m, 1H), 7.38 (td, *J* = 7.5, 2.7 Hz, 2H), 7.46-7.53 (m, 2H), 7.62-7.68 (m, 3H), 8.26 (dd, *J* = 8.0, 3.4 Hz, 1H) ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 55.5, 55.7, 103.6, 104.6 (d, *J* = 10.6 Hz), 122.6 (d, *J* = 23.0 Hz), 125.2 (d, *J* = 9.6 Hz), 127.2 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 12.5 Hz), 129.3 (d, *J* = 9.6 Hz), 130.9 (d, *J* = 103.4 Hz), 131.0 (d, *J* = 10.6 Hz), 131.7 (d, *J* = 107.4 Hz), 132.0 (d, *J* = 1.9 Hz), 133.3, 135.9 (d, *J* = 104.4 Hz), 141.4 (d, *J* = 22.1 Hz), 157.8 (d, *J* = 16.3 Hz), 162.0 (d, *J* = 16.3 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 34.8. IR (ATR): 1589 m, 1450 m, 1427 m, 1342 w, 1310 m, 1286 m, 1215 m, 1197 s, 1155 s, 1132 m, 1110 m, 1071 w, 1041 m, 999 w, 945 w, 851 m, 830 w, 788 w, 778 w, 743 s, 724 s, 691 s. MS, *m/z* (relative intensity, %): 337 (M$^+$+1, 23), 336 (M$^+$, 100), 289 (10), 288 (10), 259 (19), 243 (21). Exact Mass (EI): Calcd for $C_{20}H_{17}O_3P$ 336.0915, found 336.0914.

Mechanistic Studies (Scheme 3.5)

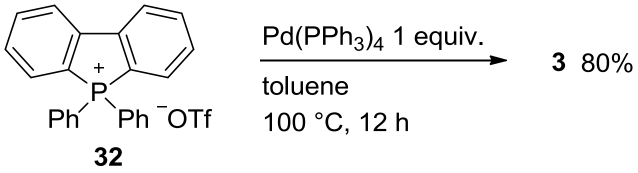
(a) Stoichiometric reaction



Palladacycle 31. Pd(OAc)$_2$ (0.22 g, 1.0 mmol) was added to a solution of **1** (0.34 g, 1.0 mmol) in toluene (16 mL). The reaction mixture was stirred at 50 °C overnight and cooled to room temperature. The solvent was concentrated and dried under vacuum to afford the palladacycle **31** (1.0 g, quantitative yield) as a white powder. Single crystals for X-ray analysis were obtained by recrystallization from hot Et$_2$O/CH$_2$Cl$_2$. The structure of **31** was determined by X-ray crystallography.

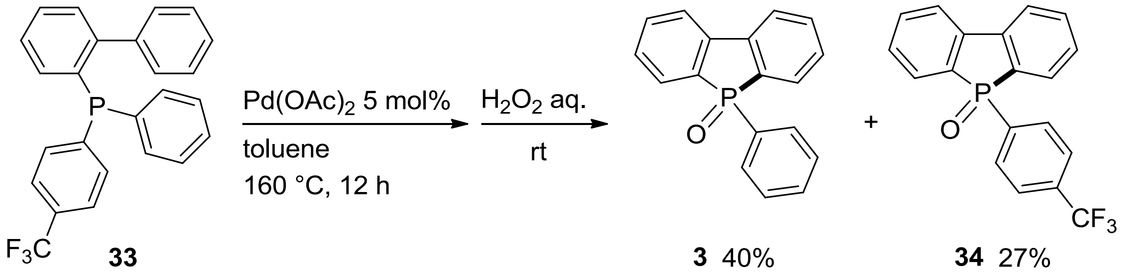
Formation of 3 from 31. An oven-dried 5 mL screw-capped vial was charged with **31** (0.10 g, 0.10 mmol) and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 100 °C for 12 h, followed by cooling. After stirring under air for 0.5 h, the mixture was purified by flash chromatography (EtOAc) to give **3**. The yield was determined by ^{1}H NMR using CHCl$_2$CHCl$_2$ as the internal standard.

(b) Intermediacy of phosphonium 32



An oven-dried 5 mL screw-capped vial was charged with **32** (73 mg, 0.15 mmol), Pd(PPh$_3$)$_4$ (0.17 g, 0.15 mmol) and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 100 °C for 12 h, followed by cooling. After stirring under air for 0.5 h, the mixture was purified by flash chromatography (EtOAc) to give **3**. The yield was determined by ^{1}H NMR using CHCl$_2$CHCl$_2$ as the internal standard. The use of Pd(OAc)$_2$ instead of Pd(PPh$_3$)$_4$ in the above reaction did not afford **3**.

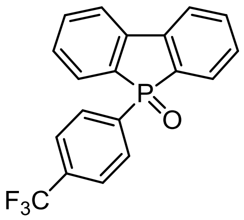
(c) Electronic effect of aryl group on phosphorus



33 → **3** 40% + **34** 27%

An oven-dried 5 mL screw-capped vial was charged with **33** (0.12 g, 0.30 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), and toluene (1 mL) under a gentle stream of nitrogen. The vessel was heated at 160 °C for 12 h, followed by cooling. An aqueous solution of H_2O_2 (ca. 30%, a few drops) was added, and the mixture was stirred at room temperature for 0.5 h. The mixture was filtered through a short pad of silica gel, and the pad was washed with EtOAc. The filtrate was evaporated, and the residue was subjected to flash chromatography (EtOAc) to give **3** (34 mg, 40%) and **34** (28 mg, 27%).

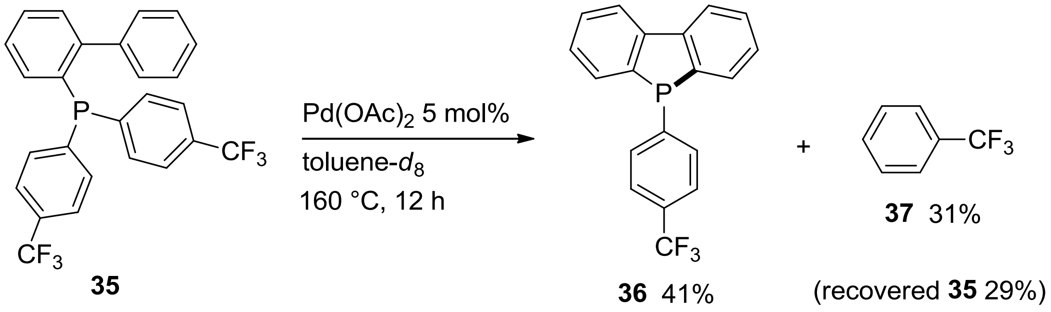
5-(4-(Trifluoromethyl)phenyl)-5*H*-dibenzophosphole 5-oxide (34)



White solid. Mp = 178 °C. Rf 0.46 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 7.40 (td, *J* = 7.5, 3.6 Hz, 2H), 7.60-7.66 (m, 4H), 7.68-7.80 (m, 4H), 7.85 (dd, *J* = 7.6, 2.8 Hz, 2H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 121.3 (d, *J* = 9.7 Hz), 123.4 (q, *J* = 272.8 Hz), 125.4-125.6 (m), 129.6 (d, *J* = 11.5 Hz), 129.8 (d, *J* = 9.6 Hz), 131.5 (d, *J* = 10.6 Hz), 131.9 (d, *J* = 107.4 Hz), 133.77 (d, *J* = 1.9 Hz), 133.79 (qd, *J* = 35.4, 1.4 Hz), 135.5 (d, *J* = 100.6 Hz), 141.7 (d, *J* = 22.0 Hz). ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 32.5. IR (ATR): 1596 w, 1472 w, 1441 w, 1396 w, 1321 s, 1204 m, 1168 s, 1126 s, 1104 s, 1080 w, 1061 s, 1016 m, 912 w, 835 m, 786 w, 758 s, 721 s. MS, *m/z* (relative intensity, %): 345 (M^++1, 21), 344 (M^+, 99), 298 (11), 297

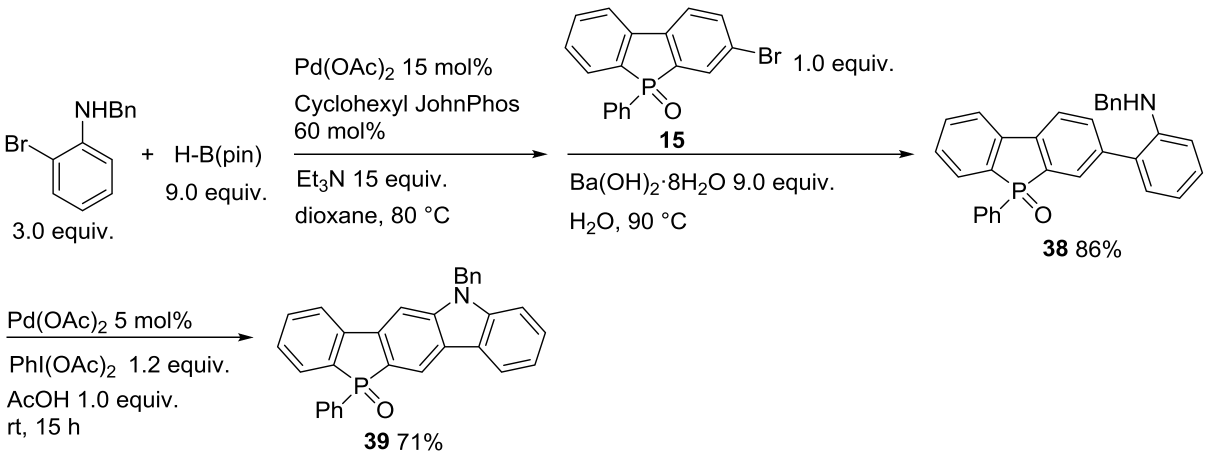
(61), 296 (19), 277 (19), 257 (11), 228 (19), 200 (13), 199 (100), 183 (72), 152 (55). Exact Mass (EI): Calcd for found $C_{19}H_{12}F_3OP$ 344.0578, found 344.0581.

(d) Fate of cleaved aryl group



An oven-dried 5 mL screw-capped vial was charged with **35** (0.14 g, 0.30 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), and toluene-d_8 (1 mL) under a gentle stream of nitrogen. The vessel was heated at 160 °C for 12 h, followed by cooling. The yields of **36**, **37**, and **35** were determined by the ^{19}F NMR spectroscopy using C_6H_5F as the internal standard. Chemical shifts (ppm) of **36**, **37** and **35** in ^{19}F NMR spectroscopy are as follows: -63.9 for **36**, -63.7 for **37**, and -63.8 for **35**.

Synthetic Elaboration of 15 (Scheme 3.6)



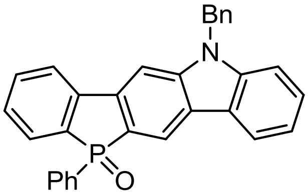
Synthesis of 38. A 20 mL two-necked flask was charged with 2-(dicyclohexylphosphino) biphenyl (32 mg, 0.090 mmol), $Pd(OAc)_2$ (5.1 mg, 0.023 mmol), 2-bromo-*N*-benzylaniline

(0.12 g, 0.45 mmol) and 2 mL of dry dioxane. Triethylamine (0.32 mL, 2.3 mmol) and pinacolborane (0.20 mL, 1.4 mmol) were then added to the mixture and stirred at 80 °C for 3 h, during which time the color changed to olive green. After cooling to room temperature, 0.3 mL of H_2O was added via syringe. $Ba(OH)_2·8H_2O$ (0.43 g, 1.4 mmol) and **13** (53 mg, 0.15 mmol) were added successively. The reaction mixture was stirred at 90 °C overnight, and then cooled to room temperature. The mixture was filtered through a Celite pad. The filtrate was dried over $MgSO_4$ and evaporated to yield the crude **38** which was further purified by flash chromatography (EtOAc) and GPC to give a white solid (59 mg, 86%).

Yellow-green solid. Mp = 95 °C. Rf 0.40 (EtOAc/Hexane = 2/1). ^{1}H NMR ($CDCl_3$, 399.78 MHz) δ: 4.30 (aps, 3H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.21-7.30 (m, 5H), 7.35-7.41 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.64-7.75 (m, 4H), 7.80-7.83 (m, 2H), 7.87 (dd, *J* = 7.6, 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100.53 MHz) δ: 48.1, 111.1, 117.3, 121.2 (d, *J* = 10.6 Hz), 121.6 (d, *J* = 10.6 Hz), 126.0, 126.95, 127.00, 128.5, 128.7 (d, *J* = 13.4 Hz), 129.2, 130.00 (d, *J* = 128.4 Hz), 130.04 (d, *J* = 7.7 Hz), 130.1 (d, *J* = 126.5 Hz), 130.5 (d, *J* = 114.0 Hz), 131.0 (d, *J* = 10.6 Hz), 132.15, 132.21 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 5.7 Hz), 133.4, 134.3, 139.1, 140.5 (d, *J* = 22.0 Hz), 140.9, 141.0, 141.5 (d, *J* = 21.0 Hz), 144.7. ^{31}P NMR ($CDCl_3$, 161.8 MHz) δ: 34.1. IR (ATR): 3420 w, 3056 w, 1597 w, 1577 w, 1509 m, 1478 w, 1451 m, 1437 m, 1397 w, 1362 w, 1320 w, 1285 w, 1192 m, 1132 w, 1111 w, 1082 w, 997 w, 837 w, 777 w, 730 s, 693 s. MS, *m/z* (relative intensity, %): 458 (M^++1, 31), 457 (M^+, 99.8), 456 (M^+-1, 100), 378 (12), 366 (11), 305 (12), 304 (14), 288 (13), 241 (11), 91 (25). Exact Mass (EI, 20 eV): Calcd for $C_{31}H_{24}NOP$ 457.1596, found 457.1597.

Synthesis of 39. The biarylamine **38** (52 mg, 0.11 mmol) and $Pd(OAc)_2$ (1.2 mg, 6.0 μmol) were stirred in toluene (6 mL) and CH_2Cl_2 (3 mL) at room temperature for 1h. $PhI(OAc)_2$ (43 mg, 0.13 mmol) and AcOH (6.0 μL, 0.11 mmol) were then added, and the reaction mixture was stirred at room temperature 15 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography (EtOAc) to give the desired product **39** (35 mg, 71%).

5-Benzyl-11-phenyl-5,11-dihydrophospholo[3,2-*b*]carbazole 11-oxide (39)



White solid. Mp = 274 °C. Rf 0.34 (EtOAc). ^{1}H NMR (CDCl$_3$, 399.78 MHz) δ: 5.57 (s, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.22-7.33 (m, 6H), 7.36-7.43 (m, 3H), 7.45-7.5 (m, 2H), 7.66-7.74 (m, 4H), 7.79 (dd, *J* = 7.8, 2.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100.53 MHz) δ: 46.7, 101.6 (d, *J* = 11.6 Hz), 109.3, 120.5, 120.9 (d, *J* = 9.6 Hz), 122.7, 122.8 (d, *J* = 11.6 Hz), 122.9 (d, *J* = 113.0 Hz), 126.2, 126.8, 127.7, 122.8, 128.6 (d, *J* = 12.5 Hz), 128.9, 129.0, 129.6 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 10.5 Hz), 131.8 (d, *J* = 104.5 Hz), 131.9 (d, *J* = 2.9 Hz), 133.1, 134.0 (d, *J* = 106.4 Hz), 136.3, 139.7, 139.9, 141.5, 142.3 (d, *J* = 21.1 Hz), 143.9. ^{31}P NMR (CDCl$_3$, 161.8 MHz) δ: 33.2. IR (ATR): 1624 w, 1595 m, 1484 m, 1462 w, 1437 m, 1357 w, 1325 m, 1266 w, 1181 s, 1131 m, 1112 m, 1070 m, 919 w, 893 w, 853 w, 763 m, 742 s, 721 s, 693 s, 658 m. MS, *m/z* (relative intensity, %): 456 (M$^+$+1, 34), 455 (M$^+$, 100), 91 (52). Exact Mass (EI): Calcd for $C_{31}H_{22}NOP$ 455.1439, found 455.1443.

3.5 References and Notes

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(2) As mentioned later, C-P bond cleavage is likely to occur through oxidative addition of a phosphonium salt. The observed selectivity is analogous to the preferential activation of aryl-X over alkyl-X in an oxidative addition process. For inertness of P-alkyl bonds in P-Ar bond cleavage reactions, see: (a) Kwong, F. Y.; Chan, K. S. *Organometallics* **2001**, *20*, 2570. (b) Ma, M.-T.; Lu, J.-M. *Tetrahedron* **2013**, *69*, 2102.

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(7) Although the stoichiometric reactions shown in Scheme 3.5a proceeded to completion at 100 °C, the catalytic reaction at 100 °C gave **3** in only 29% yield. This may suggest that excess **1** present in the catalytic setting inhibits some of the steps in the catalytic cycle and/or that catalyst regeneration is turnoverlimiting.

(8) The observed electronic effect of the aryl group on phosphorus should reflect the relative reactivities of the Ar-P bonds in the corresponding phosphonium analogous to **32**. More electrondeficient Ar-P bonds should oxidatively add to Pd(0) more easily by analogy with oxidative addition using aryl halides. Fauvarque, J.-F.; Pflüger, F.; Troupel, M. *J. Organomet. Chem.* **1981**, *208*, 419.

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Conclusion

Studies on the catalytic synthesis of heterocycles through the cleavage of carbon-heteroatom bonds are included in this thesis. The catalytic synthesis of germoles and phospholes through the cleavage of carbon-germanium and carbon-phosphrus bond is possible. The key to achieving the cleavage of carbon-heteroatom bond was revealed to be the proximity effect between the metal and the carbon-heteroatom bond.

In Chapter 1, the rhodium-catalyzed synthesis of benzogermoles via the cleavage of a carbon-germanium bond was reported. The reaction involves the activation of C(sp^3)-Ge bonds, which proceeds through an oxidative addition process.

Chapter 2 deals with the palladium-catalyzed synthesis of benzofuzed phosphacycles via carbon-phosphorus bond cleavage. The method features C-P bond cleavage, which allows for the use of tertiary phosphines as stable and readily available phosphorus sources.

Chapter 3 is concerned with the palladium-catalyzed direct synthesis of phosphole derivatives from triarylphosphines through the cleavage of carbon-hydrogen and carbon-phosphorus bonds. The reaction involves the catalytic cleavage of two inert bonds, C-H and C-P bonds, in a single catalytic cycle. Several mechanistic experiments were carried out to obtain information concerning the mechanism of this reaction.

As described in the general introduction, germole and phosphole derivatives have recently attracted significant attention as promising organic materials because of their unique optical and electronic properties. The methods reported in this thesis are improvements over previously reported methods with respect to high functional group compatibility and the stability of the starting material to air and water.

The use of proximity effect is expected to apply for the synthesis of further heterole derivatives.

This thesis was adapted from the following papers.

List of Publications

(1) Rhodium-Catalyzed Synthesis of Germoles via the Activation of Carbon-Germanium Bonds

Mamoru Tobisu, Katsuaki Baba, and Naoto Chatani

Org. Lett. **2011**, *13*, 3282-3284.

(2) Palladium-Catalyzed Direct Synthesis of Phosphole Derivatives from Triarylphosphines through Cleavage of Carbon–Hydrogen and Carbon–Phosphorus Bonds

Katsuaki Baba, Mamoru Tobisu, and Naoto Chatani

Angew. Chem., Int. Ed. **2013**, *52*, 11892-11895.

(3) Palladium-Catalyzed Synthesis of Six-Membered Benzofuzed Phosphacycles via Carbon-Phosphorus Bond Cleavage

Katsuaki Baba, Mamoru Tobisu, and Naoto Chatani

Org. Lett. **2015**, *17*, 70-73.

Supplementary List of Publications

(1) Rhodium-Catalyzed Carbon−Silicon Bond Activation for Synthesis of Benzosilole Derivatives

Masahiro Onoe, Katsuaki Baba, Yoonjoo Kim, Yusuke Kita, Mamoru Tobisu, and Naoto Chatani

J. Am. Chem. Soc. **2012**, *134*, 19477-19488.

(2) Selective Syntheses of Leuconolam, Leuconoxine, and Mersicarpine Alkaloids from a Common Intermediate through Regiocontrolled Cyclizations by Staudinger Reactions

Zining Li, Qian Geng, Zhe Lv, Beau P. Pritchett, Katsuaki Baba, Yoshitaka Numajiri, Brian M. Stoltz, and Guangxin Liang

Org. Chem. Front. Accepted

(3) Palladium-Catalyzed Synthesis of Phosphole Derivatives through Double Carbon-Phosphorus Bond Cleavage

Katsuaki Baba, Mamoru Tobisu, and Naoto Chatani

Manuscript in preparation