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Transition-Metal-Free and Base-Promoted Carbon−Heteroatom Bond Formation via C−N Cleavage of Benzyl Ammonium Salts

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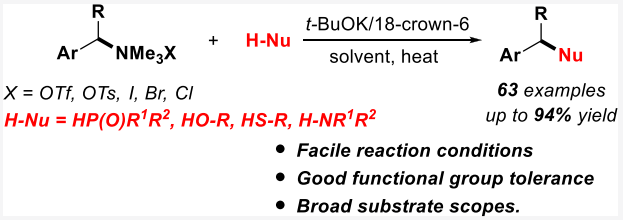
ABSTRACT: A facile and general method for constructing carbon−heteroatom (C−P, C−O, C−S, and C−N) bonds via C−N cleavage of benzyl ammonium salts under transition-metal-free conditions was reported. The combination of *t*-BuOK and 18-crown-6 enabled a wide range of substituted benzyl ammonium salts to couple readily with different kinds of heteroatom nucleophiles, i.e. hydrogen phosphoryl compounds, alcohols, thiols, and amines. Good functional group tolerance was demonstrated. The scale-up reaction and one-pot synthesis were also successfully performed.



INTRODUCTION

Amines are common fine chemicals. They are also widespread in natural products, pharmaceuticals, dyes, and functional materials. Thus, the development of methods for their transformations not only facilitates the increase of molecular complexity in methodology but also meets the requirement of late-stage modification of the related functional molecules.[1] Since the pioneering work on Ni-catalyzed cross-coupling of quaternary ammonium salts with Grignard reagents reported by Wenkert in 1988,[2] quaternary ammonium salts have attracted considerable attention as electrophiles because of the benign characteristics such as stableness and ease of preparation from amines, and the increased polarity of the C−N bond that favors the selective conversion of amines.[3] Generally, these transformations were mediated by low valent metals through C−N cleavage. Excellent studies have been reported by MacMillan,[4] Wang,[5] Watson,[6] Uchiyama,[7] and others.[8] Those works fully demonstrated the diverse reactivity and the synthetic value of quaternary ammonium salts in organic synthesis (Scheme 1A). Worth noting is that the transition-metal-free reactions forming carbon-heteroatom bonds were also achieved via base-promoted S_NAr pathway, recently (Scheme 1B).[9,10] However, the substrate scope seemed to be narrow, since only electron-deficient arylammonium salts were demonstrated in these reactions. Nevertheless, the non-use of transition-metal catalysts and associated precious ligands not only greatly reduced the cost but also avoided the metal contamination, especially for the heteroatomic compounds with coordination properties.

Along this line, we herein presented a metal-free cross-coupling of benzyl ammonium salts with heteroatom nucleophiles such as hydrogen phosphoryl compounds, alcohols, thiols, and amines, producing the corresponding valuable heteroatom products in good to high yields (Scheme 1C). Good functional group tolerance and broad substrate scopes were demonstrated. Carbon−heteroatom bonds are a key structural unit in natural and unnatural organic molecules, and thus, the development of facile and efficient methods for carbon−heteroatom bond construction is of great importance in organic synthesis.[11]

RESULTS AND DISCUSSION

Initially, benzyltrimethylammonium triflate (**1a**, 0.2 mmol) and $Ph_2P(O)H$ (**2a**, 1.2 equiv) were selected as the model reaction substrates. As shown in Table 1, the base played an important role in this reaction and the yields increased with the basicity. Thus, only a trace amount of **3a** could be detected in the absence of a base or with CsF and Na_2CO_3 (Table 1, entries 1−3). Cs_2CO_3, *t*-BuONa, and KOH also showed low reaction efficiency (Table 1, entries 4−6). When *t*-BuOK was used, a 74% yield of **3a** was obtained under similar reaction conditions (Table 1, entry 7). Since crown ethers could coordinate with alkaline metals to enhance the basicity, we envisioned that the addition of crown ethers might increase the yield. Indeed, when 1.2 equiv of 18-crown-6 was added, the yield of **3a** was increased to 84% (Table 1, entry 8). A similar positive effect was observed with *t*-BuONa (15-crown-5) and KOH (18-crown-6) (Table 1, entries 9 and 10). The loading amount of 18-crown-6 was subsequently investigated with 0.5 equiv being the best choice (Table 1, entries 11−13). As for the solvents, PhOMe was optimal, generating **3a** in 92% yield (Table 1, entry 14). This reaction could also proceed in other solvents such as cyclohexane, dioxane, THF, DMF, and DMSO (Table 1, entries

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Scheme 1. Transformations of Quaternary Ammonium Salts in Organic Synthesis

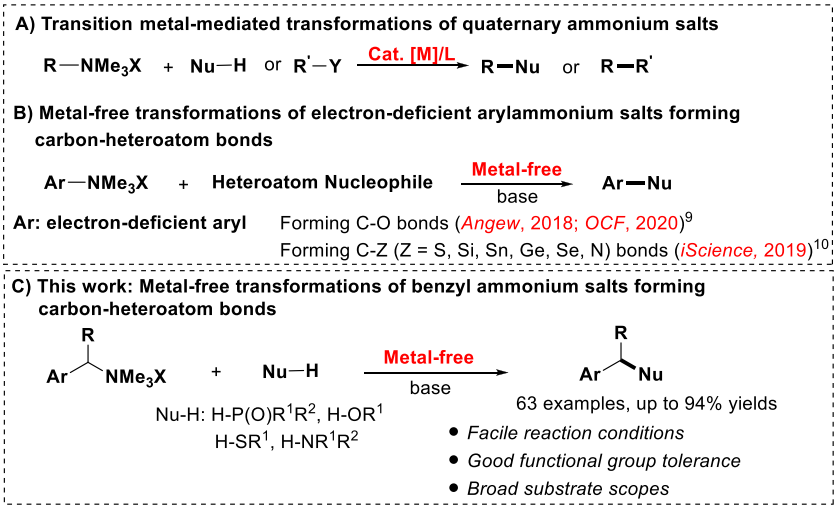
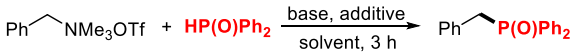


Table 1. Optimization of the Reaction Conditions[a]



entry	base	additive	solvent	temp (°C)	yield (%)[b]
1	none	none	toluene	60	trace
2	CsF	none	toluene	60	trace
3	Na_2CO_3	none	toluene	60	trace
4	Cs_2CO_3	none	toluene	60	16
5	*t*-BuONa	none	toluene	60	20
6	KOH	none	toluene	60	40
7	*t*-BuOK	none	toluene	60	74
8	*t*-BuOK	18-crown-6	toluene	60	84
9	*t*-BuONa	18-crown-6	toluene	60	67
10	KOH	15-crown-5	toluene	60	79
11[c]	*t*-BuOK	18-crown-6	toluene	60	72
12[d]	*t*-BuOK	18-crown-6	toluene	60	85
13[e]	*t*-BuOK	18-crown-6	toluene	60	78
14[d]	*t*-BuOK	18-crown-6	PhOMe	60	92
15[d]	*t*-BuOK	18-crown-6	cyclohexane	60	71
16[d]	*t*-BuOK	18-crown-6	dioxane	60	79
17[d]	*t*-BuOK	18-crown-6	THF	60	79
18[d]	*t*-BuOK	18-crown-6	DMF	60	74
19[d]	*t*-BuOK	18-crown-6	DMSO	60	66
20[d]	*t*-BuOK	18-crown-6	PhOMe	80	92
21[d]	*t*-BuOK	18-crown-6	PhOMe	40	78

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv), base (1.2 equiv), additive (1.2 equiv), solvent (2.0 mL), N_2, 60 °C, 3 h. [b]GC yield using dodecane as an internal standard. [c]*t*-BuOK (1.0 equiv), 18-crown-6 (1.0 equiv). [d]*t*-BuOK (1.2 equiv), 18-crown-6 (0.5 equiv). [e]*t*-BuOK (1.2 equiv), 18-crown-6 (0.2 equiv).

15−19). Elevating the reaction temperature to 80 °C did not enhance the reaction efficiency, while a slightly decreasing yield was given at a reduced reaction temperature (Table 1, entries 20 and 21).

With the optimized conditions in hand, the substrate scopes were subsequently examined (Tables 2 and 3). This reaction seemed rather general for both benzylic ammonium salts and nucleophiles. Thus, in addition to **1a**, benzylic ammonium triflates bearing electron-donating groups such as −^{t}Bu, −Me, and −OMe at the benzene ring, regardless of their position, were all applicable to this reaction, producing the corresponding products in 90−93% yields (**3b−g**). Derivatives with an oxygen-containing heterocycle and π-extended frameworks also worked well under the reaction conditions (**3h−j**). Halogen groups (−F, −Cl, −Br) were compatible in the current reaction system, facilitating further functionalization via cross-coupling (**3k−o**). Worth noting is that the bromo group did not survive in the reported nickel and palladium catalytic systems due to the high reactivity of the C_{Ar}−Br bond,[5g,8l] its tolerance under the present conditions highlighting the advantage of this reaction (**3n** and **3o**). Substrates bearing electron-withdrawing groups such as the $-CF_3$, −CN, and ester group at the benzene ring also served well, furnishing the expected products in high yields (Table 2, **3p−r**). However, the branched fluorenyl ammonium triflate gave a relatively low yield under the reaction conditions. The result might be ascribed to the rigid steric hindrance. Especially, a very low yield of **3t** was obtained with the 1-phenylethylammonium triflate due to the competing generation of styrene.

As for the hydrogen phosphoryl compounds, all the substrates bearing groups such as the −Me, −OMe, $-NMe_2$, −Cl, and phenyl group at the benzene ring showed high reactivity in the current reaction system, delivering the desired organophosphorus compounds in 60−90% yields (**3u−za**). However, when butyl(phenyl)phosphine oxide was used, only a 42% yield of **3zb** was obtained under similar reaction conditions. A relatively low yield was also given with a dialkylphosphine oxide such as ^{n}Bu$_2$P(O)H (**3zc**). Probably because of the easy hydrolysis under strongly alkaline conditions, no desired product was observed with *H*-phosphonate (not shown in the table). The counterion effect was subsequently investigated (Scheme 2). Besides OTf^-, other counter-anions such as OTs^-, I^-, Br^-, and Cl^- were also workable. These results well demonstrated the generality of this reaction.

By simply replacing the solvent with toluene and elevating the reaction temperature to 120 °C, this reaction was readily extended to other heteroatomic nucleophiles (Table 3). Phenols with both electron-donating and electron-withdrawing groups underwent the S_N reaction smoothly, giving the desired benzyl aryl ethers in good to excellent yields (**5a−l**). Steric hindrance seemed not to affect the reaction. For example, when 2-phenylphenol was allowed to react with **1a**, the etherification product **5e** was afforded in 94% yield. Halogen groups including −F, −Cl, −Br, and even −I were compatible, furnishing the

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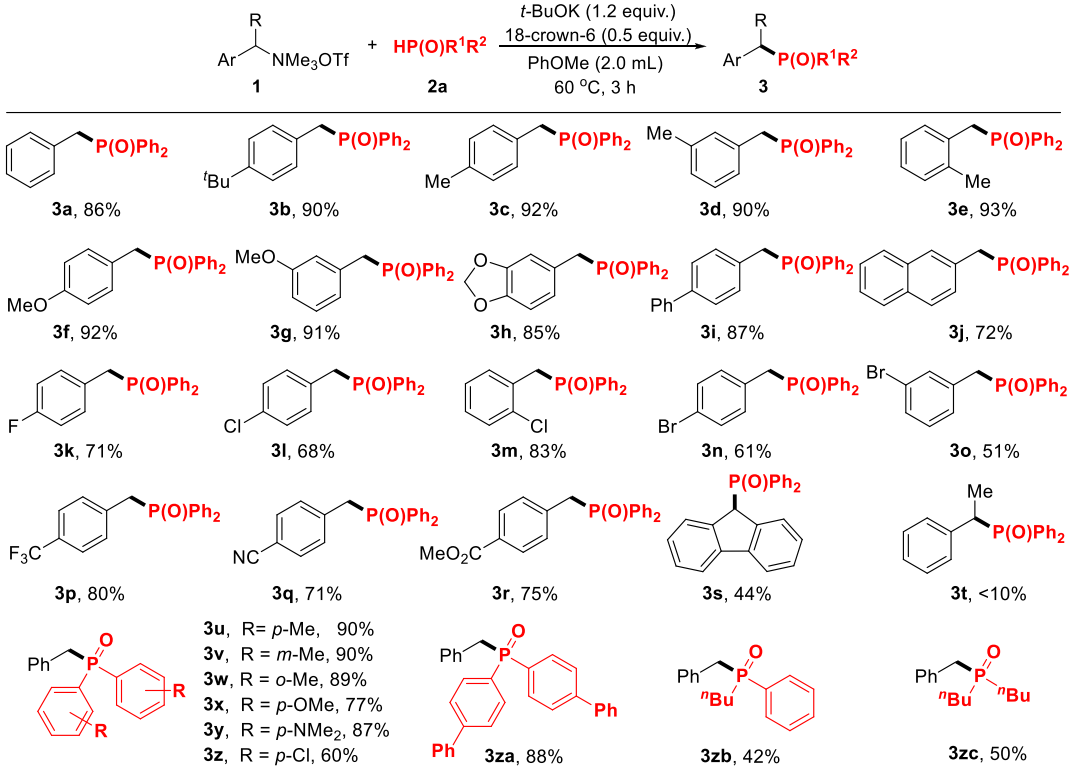
Table 2. Scope of Benzyl Ammonium Salts and P(O)H Compounds[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (1.2 equiv), *t*-BuOK (1.2 equiv), 18-crown-6 (0.5 equiv), PhOMe (2.0 mL), N_2, 60 °C, 3 h. Isolated yield.

corresponding products in good yields (**5f**–**i**). These results also provided the possibility of constructing more complex molecules from these products. 2-Naphthol and 1-naphthols including those having a functional group were also converted into the expected aromatic ethers in good to high yields (**5m**–**p**). Alcohols such as benzyl alcohol, furfuryl alcohol, and perillyl alcohol were also found to be effective under the present reaction conditions (**5q**–**s**); however, no desired product was obtained when *i*-PrOH was used (**5t**).

Regarding the similarity to alcohols, we then turned our attention to investigate thiophenols. Again, both electron-rich and electron-deficient thiophenols gave the corresponding products **6a**–**e** in good yields. 2-Naphthalenethiol and heterocyclic thiophenethiol produced **6f** and **6g** in 91% and 73% yields under the reaction conditions, respectively. Aliphatic mercaptans could also be converted to the corresponding products in good yields (**6h** and **6i**). In addition to thiophenols, amines such as indoles, phenothiazine, carbazole, and benzimidazole also served as the right substrates, furnishing the desired products in 48–86% yields (**7a**–**f**). Simple aniline was also applicable. For example, the reaction of diphenylamine with **1a** afforded N-benzyl-*N*-phenylaniline **7g** in 63% yield by the strategy.[12] Unfortunately, aliphatic amines seemed not to be suitable to this reaction (**7h**).

To further evaluate the synthetic applicability of this method, scale-up reactions between **1a** and **4e** were performed on 2 and 10 mmol scales, and the corresponding product **5e** was obtained in 90% and 81% yields, respectively (Scheme 3, eq 1). Considering that quaternary ammonium salts can be easily generated from amines, we wondered if one-pot synthesis, in which ammonium salts was generated in situ from amines, is feasible; if successful, the synthetic scheme would be greatly shorter, thus enhancing the synthetic efficiency. To our delight, when *N*,*N*-dimethylbenzylamine (**1A**) was used as the starting material, **5e** could also be obtained in 88% yield with 1.2 equiv MeOTf as an additive (Scheme 3, eq 2). These results described above well demonstrated the synthetic value of this reaction in organic synthesis.

In order to gain some insight into the mechanism, several control experiments were performed (Scheme 4). When benzyltrimethylammonium triflate **1a** was allowed to react with phenol potassium **4e′** in the absence of *t*-BuOK and 18-crown-6, an 89% yield of **5e** was obtained (Scheme 4, eq 1). A higher yield of 96% was obtained when 0.5 equiv of 18-crown-6 was added (Scheme 4, eq 2). However, when additional *t*-BuOK (1.2 euqiv) was added to the reaction, only a 13% yield of **5e** was obtained (Scheme 4, eq 3).[13] These results indicated that *t*-BuOK acted as a base to promote the generation of active KNu, which then underwent nucleophilic substitution to benzyl ammonium salts to produce the corresponding products. The 18-crown-6 might coordinate with K^+ to release Nu^-, thus promoting this transformation.

■ CONCLUSIONS

In conclusion, we developed a combination of *t*-BuOK and 18-crown-6 to enable the transition-metal-free transformation of benzyl ammonium salts via C–N bond cleavage. A wide range of benzyl ammonium salts coupled readily with various heteroatom nucleophiles such as hydrogen phosphoryl compounds, alcohols, thiols, and amines, representing a relatively general carbon–heteroatom bond-forming reaction. The scale-up experiment and one-pot synthesis also demonstrated the utility of this reaction in organic synthesis.

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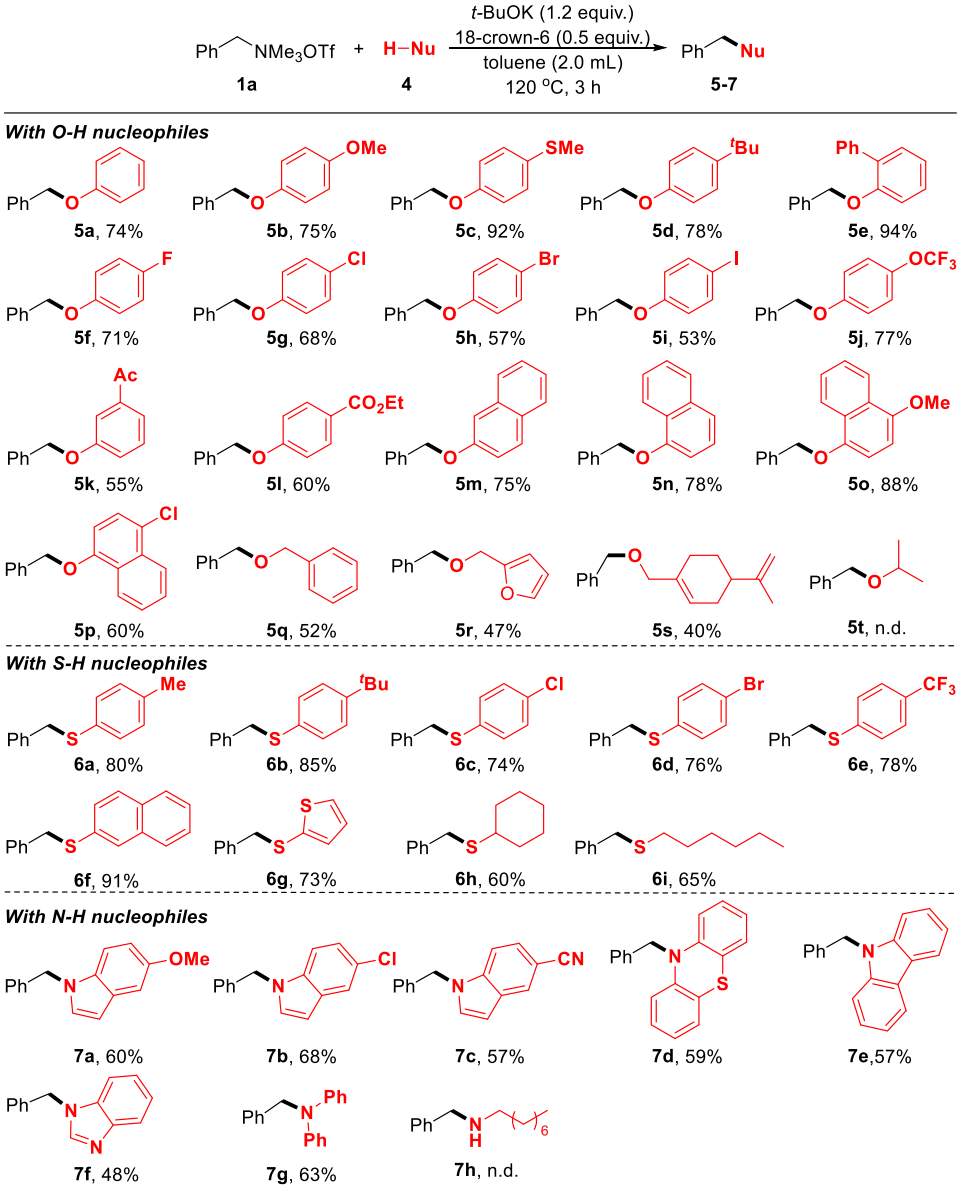
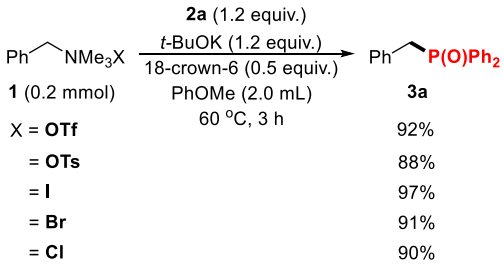
Table 3. Scope of Heteroatomic Nucleophiles[a]



[a]Reaction conditions: **1a** (0.2 mmol), **4** (1.2 equiv), *t*-BuOK (1.2 equiv), 18-crown-6 (0.5 equiv), toluene (2.0 mL), N_2, 120 °C, 3 h. Isolated yield.

Scheme 2. Investigation of the Counterion Effect



EXPERIMENTAL SECTION

General Information. The reactions were carried out in Schlenk tubes of 25 mL under a N_2 atmosphere. For reactions that require heating, the heating mantle was used as the heat source. Benzyl ammonium salts were prepared according to the reported literature.[6a] $HP(O)R_2$ (R = *p*-Me-C_6H_4, *m*-Me-C_6H_4, *o*-Me-C_6H_4, *p*-Me-OC_6H_4, *p*-Me_2N-C_6H_4, *p*-Cl-C_6H_4, and *p*-Ph-C_6H_4, *n*-Bu) were prepared according to the literature procedures.[14] $HP(O)Ph_2$, $HP(O)(O^iPr)_2$, and other reagents (phenols, alcohols, thiophenols, mercaptans, amines) were used as received, and solvents were purified according to standard operation procedures. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin. Column chromatography was performed using Silica Gel 60 (300−400 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2014. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400, 100, and 162 MHz, respectively, and chemical shifts were reported in parts per million (ppm). HRMS data were recorded on an LCMS-IT-TOF instrument by the ESI technique.

General Experimental Procedure I. An oven-dried 25 mL Schlenk tube was charged with benzyl ammonium triflates **1** (0.2 mmol), P(O)H compounds **2** (0.24 mmol), *t*-BuOK (0.24 mmol, 1.2 equiv), and 18-crown-6 (0.1 mmol, 0.5 equiv). After charging with N_2 three times, PhOMe (2.0 mL) was added. The reaction mixture was reacted at 60 °C for 3 h. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was

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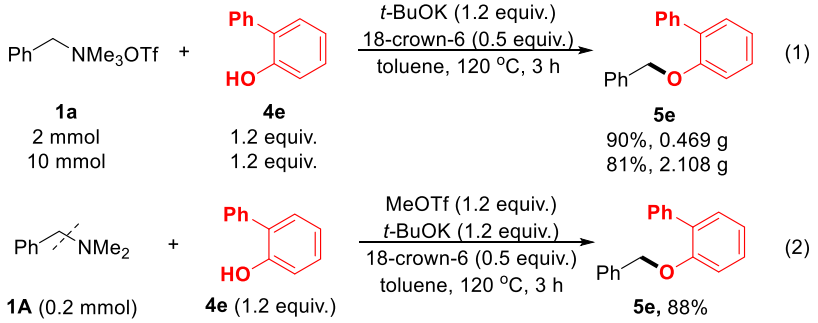
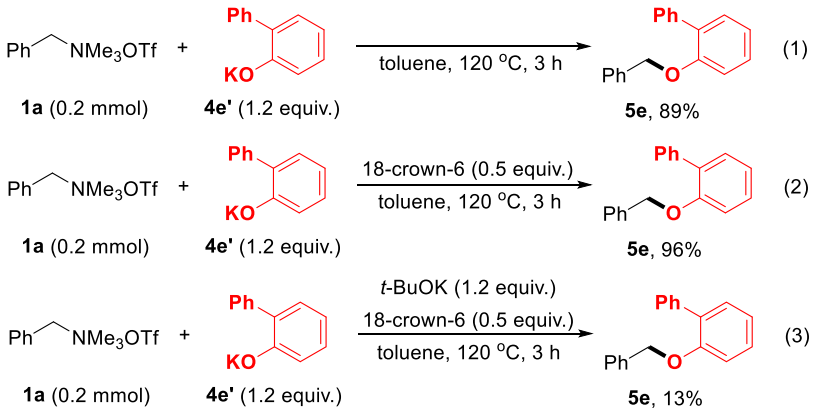
Scheme 3. Scale-up and One-pot Synthesis



Scheme 4. Control Experiments



isolated by column chromatography over silica gel (300−400 mesh) using petroleum ether-ethyl acetate (PE-EA) or dichloromethane-ethyl acetate (DCM-EA) as eluent.

General Experimental Procedure II. An oven-dried 25 mL Schlenk tube was charged with benzyl ammonium triflates **1a** (0.2 mmol), nucleophiles **4** (0.24 mmol, if it is liquid, added after charging N_2), *t*-BuOK (0.24 mmol, 1.2 equiv), and 18-crown-6 (0.1 mmol, 0.5 equiv). After charging with N_2 three times, toluene (2.0 mL) was added. The reaction mixture was reacted at 120 °C for 3 h. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (300−400 mesh) using PE-EA as eluent. This experimental procedure is suited for nucleophiles such as H−OR, H−SR, and H−NR_1R_2.

Procedure for the Preparation of 5e on 2 mmol Scale. An oven-dried 100 mL Schlenk tube was charged with benzyl ammonium triflates **1a** (2 mmol), 2-phenylphenol **4e** (2.4 mmol, 1.2 equiv), *t*-BuOK (2.4 mmol, 1.2 equiv), and 18-crown-6 (1 mmol, 0.5 equiv). After charging with N_2 three times, toluene (20 mL) was added. The reaction mixture was reacted at 120 °C for 3 h. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (300−400 mesh) using PE as eluent to afford a colorless oil in 90% yield (0.469 g).

Benzyldiphenylphosphine Oxide (3a). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 86% yield (50.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 4H), 7.45−7.41 (m, 2H), 7.38−7.34 (m, 4H), 7.12−7.09 (m, 3H), 7.04−7.01 (m, 2H), 3.58 (d, J = 14.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 132.2 (d, J_{C-P} = 98.5 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 130.1 (d, J_{C-P} = 5.2 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 128.3 (d, J_{C-P} = 2.4 Hz), 126.7 (d, J_{C-P} = 2.9 Hz), 38.0 (d, J_{C-P} = 66.1 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[81]

(4-(*tert*-Butyl)benzyl)diphenylphosphine Oxide (3b). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 90% yield (62.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 4H), 7.43−7.39 (m, 2H), 7.36−7.32 (m, 4H), 7.12 (d, J = 8.2 Hz, 2H), 6.95 (dd, J_1 = 8.4 Hz, J_2= 2.4 Hz, 2H), 3.55 (d, J = 13.6 Hz, 2H), 1.17 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.5 (d, J_{C-P} = 3.4 Hz), 132.3 (d, J_{C-P}=98.1 Hz),131.7 (d, J_{C-P}=2.7 Hz), 131.1 (d, J_{C-P} = 8.9 Hz), 129.7 (d, J_{C-P} = 5.2 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 127.8 (d, J_{C-P} = 7.9 Hz), 125.3 (d, J_{C-P} = 2.4 Hz), 37.4 (d, J_{C-P}=66.5 Hz), 34.3, 31.2. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[81]

(4-Methylbenzyl)diphenylphosphine Oxide (3c). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 92% yield (56.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 4H), 7.44−7.40 (m, 2H), 7.38−7.33 (m, 4H), 6.91 (s, 4H), 3.54 (d, J = 13.6 Hz, 2H), 2.18 (d, J = 1.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 136.3 (d, J_{C-P} = 2.9 Hz), 132.4 (d, J_{C-P} = 98.2 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 131.1 (d, J_{C-P} = 8.9 Hz), 129.9 (d, J_{C-P} = 5.1 Hz), 129.1 (d, J_{C-P} = 2.1 Hz), 128.4 (d, J_{C-P} = 11.5 Hz), 127.8 (d, J_{C-P} = 8.0 Hz), 37.6 (d, J_{C-P} = 66.5 Hz), 21.0. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.5. This compound is known.[81]

(3-Methylbenzyl)diphenylphosphine Oxide (3d). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 90% yield (55.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.59 (m, 4H), 7.45−7.41 (m, 2H), 7.38−7.34 (m, 4H), 7.00−6.97 (m, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.84 (s, 1H), 6.79 (d, J = 7.2 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H), 2.14 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.9 (d, J_{C-P} = 2.5 Hz), 132.3 (d, J_{C-P} = 98.3 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.2 (d, J_{C-P} = 9.0 Hz), 131.0 (d, J_{C-P} = 5.2 Hz), 130.9 (d, J_{C-P} = 7.9 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 128.1 (d, J_{C-P} = 2.5 Hz), 127.5 (d, J_{C-P} = 3.0 Hz), 127.0 (d, J_{C-P} = 5.3 Hz), 38.0 (d, J_{C-P} = 66.2 Hz), 21.2. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.5. This compound is known.[81]

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(2-Methylbenzyl)diphenylphosphine Oxide (3e). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 93% yield (57.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.57 (m, 4H), 7.46−7.42 (m, 2H), 7.37−7.33 (m, 4H), 7.01−7.00 (m, 2H), 6.93−6.86 (m, 2H), 3.59 (d, J = 14.0 Hz, 2H), 2.06 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.4 (d, J_{C-P} = 5.2 Hz), 132.3 (d, J_{C-P} = 98.8 Hz), 131.8 (d, J_{C-P} = 2.4 Hz), 131.2 (d, J_{C-P} = 8.9 Hz), 130.7 (d, J_{C-P} = 4.4 Hz), 130.4 (d, J_{C-P} = 2.5 Hz), 129.6 (d, J_{C-P} = 8.1 Hz), 128.4 (d, J_{C-P} = 11.5 Hz), 126.9 (d, J_{C-P} = 2.9 Hz), 125.7 (d, J_{C-P} = 2.6 Hz), 35.2 (d, J_{C-P} = 66.3 Hz), 20.0. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[81]

(4-Methoxybenzyl)diphenylphosphine Oxide (3f). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 92% yield (59.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.58 (m, 4H), 7.44−7.40 (m, 2H), 7.37−7.33 (m, 4H), 6.95−6.93 (m, 2H), 6.65 (d, J = 8.4 Hz, 2H), 3.65 (s, 3H), 3.51 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.4 (d, J_{C-P} = 2.7 Hz), 132.3 (d, J_{C-P} = 97.9 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 131.0 (d, J_{C-P} = 4.9 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 122.8 (d, J_{C-P} = 8.0 Hz), 113.8 (d, J_{C-P} = 2.3 Hz), 55.1, 37.0 (d, J_{C-P} = 67.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known.[81]

(3-Methoxybenzyl)diphenylphosphine Oxide (3g). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 91% yield (58.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 4H), 7.47−7.43 (m, 2H), 7.40−7.35 (m, 4H), 7.02 (t, J = 8.0 Hz, 1H), 6.66−6.61 (m, 2H), 6.56 (s, 1H), 3.57 (s, 3H), 3.57 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4 (d, J_{C-P} = 2.2 Hz), 132.5 (d, J_{C-P} = 7.9 Hz), 132.2 (d, J_{C-P} = 98.7 Hz), 131.8 (d, J_{C-P} = 2.1 Hz), 131.2 (d, J_{C-P} = 8.9 Hz), 129.3 (d, J_{C-P} = 2.0 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 122.6 (d, J_{C-P} = 5.2 Hz), 115.2 (d, J_{C-P} = 5.0 Hz), 113.0 (d, J_{C-P} = 2.6 Hz), 55.1, 38.2 (d, J_{C-P} = 66.8 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known.[15]

(Benzo[d][1,3]dioxol-5-ylmethyl)diphenylphosphine Oxide (3h). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 85% yield (57.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.60 (m, 4H), 7.43 (d, J = 6.8 Hz, 2H), 7.38 (d, J = 6.8 Hz, 4H), 6.57−6.53 (m, 2H), 6.45 (d, J = 7.2 Hz, 1H), 5.80 (s, 2H), 3.49 (d, J = 13.2 Hz, 2H), 1.98 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.5 (d, J_{C-P} = 1.8 Hz), 146.5 (d, J_{C-P} = 2.8 Hz), 132.2 (d, J_{C-P} = 98.1 Hz), 131.8 (d, J_{C-P} = 2.3 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 128.5 (d, J_{C-P} = 11.5 Hz), 124.4 (d, J_{C-P} = 8.1 Hz), 123.3 (d, J_{C-P} = 6.1 Hz), 110.5 (d, J_{C-P} = 4.7 Hz), 108.1 (d, J_{C-P} = 2.2 Hz), 100.9, 37.6 (d, J_{C-P} = 67.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.5. This compound is known.[81]

([1,1′-Biphenyl]-4-ylmethyl)diphenylphosphine Oxide (3i). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with DCM:EA = 4:1 (v/v) to afford a white solid in 87% yield (64.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75−7.70 (m, 4H), 7.54−7.50 (m, 4H), 7.47−7.38 (m, 8H), 7.33−7.29 (m, 1H), 7.17 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 3.70 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.6 (d, J_{C-P} = 1.2 Hz), 139.6 (d, J_{C-P} = 3.1 Hz), 132.2 (d, J_{C-P} = 98.5 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.5 (d, J_{C-P} = 5.2 Hz), 130.1 (d, J_{C-P} = 8.1 Hz), 128.7, 128.5 (d, J_{C-P} = 11.7 Hz), 127.2, 127.1 (d, J_{C-P} = 2.6 Hz), 126.9, 37.8 (d, J_{C-P} = 66.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known.[16]

(Naphthalen-2-ylmethyl)diphenylphosphine Oxide (3j). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 72% yield (49.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.56 (m, 7H), 7.48 (s, 1H), 7.43−7.39 (m, 2H), 7.35−7.29 (m, 6H), 7.15 (d, J = 8.4 Hz, 1H), 3.72 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2 (d, J_{C-P} = 2.3 Hz), 132.2 (d, J_{C-P} = 98.4 Hz), 132.1 (d, J_{C-P} = 2.1 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 128.9 (d, J_{C-P} = 6.7 Hz), 128.7 (d, J_{C-P} = 8.2 Hz), 128.5 (d, J_{C-P} = 11.7 Hz), 128.1 (d, J_{C-P} = 4.2 Hz), 127.9 (d, J_{C-P} = 1.9 Hz), 127.6 (d, J_{C-P} = 0.9 Hz), 127.5 (d, J_{C-P} = 1.1 Hz), 125.9, 125.6 (d, J_{C-P} = 0.9 Hz), 38.3 (d, J_{C-P} = 65.9 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.5. This compound is known.[81]

(4-Fluorobenzyl)diphenylphosphine Oxide (3k). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 71% yield (44.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.58 (m, 4H), 7.46−7.42 (m, 2H), 7.39−7.34 (m, 4H), 7.01−6.97 (m, 2H), 6.81−6.77 (m, 2H), 3.54 (d, J = 13.2 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.8 (dd, J_{1C-P} = 244.0 Hz, J_{2C-P} = 3.4 Hz), 132.0 (d, J_{C-P} = 98.5 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.5 (dd, J_{1C-P} = 8.0 Hz, J_{2C-P} = 5.3 Hz), 131.0 (d, J_{C-P} = 9.0 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 126.7 (dd, J_{1C-P} = 8.0 Hz, J_{2C-P} = 3.1 Hz), 115.2 (dd, J_{1C-P} = 21.2 Hz, J_{2C-P} = 2.3 Hz), 37.1 (d, J_{C-P} = 66.4 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.4. This compound is known.[81]

(4-Chlorobenzyl)diphenylphosphine Oxide (3l). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 68% yield (44.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 4H), 7.48−7.44 (m, 2H), 7.40−7.36 (m, 4H), 7.09 (d, J = 8.4 Hz, 2H), 6.98−6.95 (m, 2H), 3.54 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 132.8 (d, J_{C-P} = 3.6 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.9 (d, J_{C-P} = 99.0 Hz), 131.4 (d, J_{C-P} = 5.3 Hz), 131.1, (d, J_{C-P} = 9.1 Hz), 129.6 (d, J_{C-P} = 8.0 Hz), 128.6 (d, J_{C-P} = 11.7 Hz), 128.5 (d, J_{C-P} = 2.2 Hz), 37.4 (d, J_{C-P} = 65.8 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.3. This compound is known.[81]

(2-Chlorobenzyl)diphenylphosphine Oxide (3m). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 83% yield (54.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.60 (m, 4H), 7.48−7.40 (m, 3H), 7.37−7.32 (m, 4H), 7.14 (d, J = 8.0 Hz, 1H), 7.10−7.01 (m, 2H), 3.79 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.2 (d, J_{C-P} = 7.0 Hz), 132.0 (d, J_{C-P} = 99.2 Hz), 131.9 (d, J_{C-P} = 4.4 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 9.2 Hz), 129.6 (d, J_{C-P} = 7.3 Hz), 129.3 (d, J_{C-P} = 2.2 Hz), 128.4 (d, J_{C-P} = 11.7 Hz), 128.2 (d, J_{C-P} = 2.7 Hz), 126.8 (d, J_{C-P} = 2.5 Hz), 34.5 (d, J_{C-P} = 66.2 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.5. This compound is known.[81]

(4-Bromobenzyl)diphenylphosphine Oxide (3n). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 61% yield (45.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.69 (m, 4H), 7.56−7.48 (m, 6H), 7.33 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 3.63 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 132.0 (d, J_{C-P} = 2.4 Hz), 131.8 (d, J_{C-P} = 98.9 Hz), 131.7 (d, J_{C-P} = 5.1 Hz), 131.4 (d, J_{C-P} = 2.3 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.1 (d, J_{C-P} = 8.0 Hz), 128.6 (d, J_{C-P} = 11.7 Hz), 120.9 (d, J_{C-P} = 3.9 Hz), 37.5 (d, J_{C-P} = 65.8 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.3. This compound is known.[16]

(3-Bromobenzyl)diphenylphosphine Oxide (3o). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 51% yield (37.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 4H), 7.48−7.43 (m, 2H), 7.41−7.36 (m, 4H), 7.24−7.21 (m, 1H), 7.11 (d, J = 1.6 Hz, 1H), 7.02−6.96 (m, 2H), 3.53 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.4 (d, J_{C-P} = 7.9 Hz), 133.0 (d, J_{C-P} = 5.2 Hz), 131.8 (d, J_{C-P} = 99.2 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 129.8 (d, J_{C-P} = 2.4 Hz), 128.7 (d, J_{C-P} = 5.0 Hz), 128.6 (d, J_{C-P} = 11.8 Hz), 122.2 (d, J_{C-P} = 2.9 Hz), 37.7 (d, J_{C-P} = 65.3 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.3. This compound is known.[17]

Diphenyl(4-(trifluoromethyl)benzyl)phosphine Oxide (3p). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on

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silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 80% yield (57.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J_1= 11.2, J_2= 7.2 Hz, 4H), 7.46 (t, J = 7.2 Hz, 2H), 7.40−7.35 (m, 6H), 7.15 (d, J = 8.0 Hz, 2H), 3.63 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.4 (d, J_{C-P} = 9.0 Hz), 132.0 (d, J_{C-P} = 2.9 Hz), 131.8 (d, J_{C-P} = 100.3 Hz), 131.0 (d, J_{C-P} = 9.3 Hz), 130.3 (d, J_{C-P} = 5.3 Hz), 129.0 (dd, J_{1C-P} = 32.0 Hz, J_{2C-P} = 3.0 Hz), 128.6 (d, J_{C-P} = 11.9 Hz), 125.3−125.1 (m), 124.1 (q, J_{C-P} = 271.3 Hz), 38.0 (d, J_{C-P} = 64.6 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.1. This compound is known.[81]

4-((Diphenylphosphoryl)methyl)benzonitrile (3q). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 71% yield (45.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.58 (m, 4H), 7.49−7.44 (m, 2H), 7.41−7.36 (m, 6H), 7.14 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 3.62 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.1 (d, J_{C-P} = 8.0 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.0 (d, J_{C-P} = 9.2 Hz), 130.7 (d, J_{C-P} = 5.1 Hz), 128.7 (d, J_{C-P} = 11.8 Hz), 118.7 (d, J_{C-P} = 1.7 Hz), 110.6 (d, J_{C-P} = 3.1 Hz), 38.4 (d, J_{C-P} = 63.9 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 28.9. This compound is known.[81]

Methyl 4-((Diphenylphosphoryl)methyl)benzoate (3r). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with DCM:EA = 3:1 (v/v) to afford a white solid in 75% yield (52.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 2H), 7.71−7.66 (m, 4H), 7.54−7.52 (m, 2H), 7.47−7.43 (m, 4H), 7.18 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 3.87 (s, 3H), 3.70 (d, J = 14.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.9 (d, J_{C-P} = 1.1 Hz), 136.7 (d, J_{C-P} = 8.0 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 99.2 Hz), 131.1 (d, J_{C-P} = 9.2 Hz), 130.1 (d, J_{C-P} = 5.1 Hz), 129.6 (d, J_{C-P} = 2.5 Hz), 128.6 (d, J_{C-P} = 11.7 Hz), 52.0, 38.3 (d, J_{C-P} = 64.7 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.1. This compound is known.[18]

(9H-Fluoren-9-yl)diphenylphosphine Oxide (3s). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with DCM:EA = 5:1 (v/v) to afford a white solid in 44% yield (32.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.6 Hz, 2H), 7.49−7.39 (m, 6H), 7.34−7.30 (m, 6H), 7.26−7.24 (m, 2H), 7.15 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 2H), 5.13 (d, J = 23.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.8 (d, J_{C-P} = 4.7 Hz), 139.0 (d, J_{C-P} = 3.9 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 8.8 Hz), 129.9 (d, J_{C-P} = 99.2 Hz), 128.2 (d, J_{C-P} = 11.7 Hz), 127.7 (d, J_{C-P} = 2.0 Hz), 126.8 (d, J_{C-P} = 2.2 Hz), 126.1 (d, J_{C-P} = 2.8 Hz), 119.9, 50.6 (d, J_{C-P} = 61.6 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 33.6. This compound is known.[19]

Benzyldi-*p*-tolylphosphine Oxide (3u). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 90% yield (57.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.45 (m, 4H), 7.16−7.13 (m, 4H), 7.10−7.07 (m, 3H), 7.04−7.01 (m, 2H), 3.53 (d, J = 14.0 Hz, 2H), 2.29 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.1 (d, J_{C-P} = 2.6 Hz), 132.0 (d, J_{C-P} = 10.1 Hz), 131.4 (d, J_{C-P} = 6.9 Hz), 131.1 (d, J_{C-P} = 9.4 Hz), 130.1 (d, J_{C-P} = 5.3 Hz), 129.1 (d, J_{C-P} = 11.9 Hz), 129.0 (d, J_{C-P} = 101.0 Hz), 128.2 (d, J_{C-P} = 2.4 Hz), 126.6 (d, J_{C-P} = 2.9 Hz), 38.2 (d, J_{C-P} = 66.2 Hz), 21.5. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.9. This compound is known.[81]

Benzyldi-*m*-tolylphosphine Oxide (3v). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 90% yield (57.6 mg), mp: 167.7−169.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 12.0 Hz, 2H), 7.38−7.34 (m, 2H), 7.23−7.18 (m, 4H), 7.11−7.05 (m, 3H), 7.03−7.01 (m, 2H), 3.53 (d, J = 14.0 Hz, 2H), 2.23 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2 (d, J_{C-P} = 11.4 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 97.9 Hz), 131.6 (d, J_{C-P} = 8.6 Hz), 131.2 (d, J_{C-P} = 7.9 Hz), 130.0 (d, J_{C-P} = 5.2 Hz), 128.2 (d, J_{C-P} = 3.4 Hz), 128.1 (d, J_{C-P} = 6.5 Hz), 127.8 (d, J_{C-P} = 9.5 Hz), 126.5 (d, J_{C-P} = 2.9 Hz), 37.9 (d, J_{C-P} = 65.9 Hz), 21.2. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.7. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{21}H_{22}OP$, 321.1408; found, 321.1409.

Benzyldi-*o*-tolylphosphine Oxide (3w). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 89% yield (57.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.48 (m, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.6 Hz, 2H), 7.10−7.07 (m, 5H), 6.98−6.95 (m, 2H), 3.67 (d, J = 13.6 Hz, 2H), 2.13 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.2 (d, J_{C-P} = 8.0 Hz), 131.7 (d, J_{C-P} = 9.5 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 131.4 (d, J_{C-P} = 10.8 Hz), 131.3 (d, J_{C-P} = 95.8 Hz), 131.1 (d, J_{C-P} = 7.5 Hz), 130.3 (d, J_{C-P} = 5.1 Hz), 128.1 (d, J_{C-P} = 2.5 Hz), 126.6 (d, J_{C-P} = 2.9 Hz), 125.4 (d, J_{C-P} = 11.9 Hz), 37.3 (d, J_{C-P} = 65.8 Hz), 21.0 (d, J_{C-P} = 4.0 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 31.5. This compound is known.[20]

Benzylbis(4-methoxyphenyl)phosphine Oxide (3x). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with DCM:EA = 1:1 (v/v) to afford a white solid in 77% yield (54.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.48 (m, 4H), 7.13−7.10 (m, 3H), 7.02−7.00 (m, 2H), 6.86 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 3.76 (s, 6H), 3.52 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J_{C-P} = 2.6 Hz), 133.0 (d, J_{C-P} = 10.4 Hz), 131.6 (d, J_{C-P} = 7.8 Hz), 130.1 (d, J_{C-P} = 5.1 Hz), 128.3 (d, J_{C-P} = 2.3 Hz), 126.6 (d, J_{C-P} = 2.8 Hz), 123.7 (d, J_{C-P} = 104.8 Hz), 114.0 (d, J_{C-P} = 12.6 Hz), 55.3, 38.6 (d, J_{C-P} = 67.1 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known.[21]

Benzylbis(4-(dimethylamino)phenyl)phosphine Oxide (3y). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with DCM:EA = 1:1 (v/v) to afford a white solid in 87% yield (65.8 mg), mp: 236.3−237.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J_1 = 10.8 Hz, J_2 = 8.8 Hz, 4H), 7.12−7.03 (m, 5H), 6.59 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 4H), 3.47 (d, J = 14.0 Hz, 2H), 2.91 (s, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.1 (d, J_{C-P} = 2.2 Hz), 132.6 (d, J_{C-P} = 6.2 Hz), 132.5 (d, J_{C-P} = 10.2 Hz), 130.2 (d, J_{C-P} = 5.1 Hz), 128.1 (d, J_{C-P} = 2.5 Hz), 126.2 (d, J_{C-P} = 2.8 Hz), 117.9 (d, J_{C-P} = 109.2 Hz), 111.1 (d, J_{C-P} = 12.4 Hz), 39.9, 38.9. ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 30.6. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{23}H_{28}N_2OP$, 379.1939; found, 379.1936.

Benzylbis(4-chlorophenyl)phosphine Oxide (3z). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 60% yield (43.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.50 (m, 4H), 7.36 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 4H), 7.15−7.13 (m, 3H), 7.03−7.01 (m, 2H), 3.56 (d, J = 14.0 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.7 (d, J_{C-P} = 3.2 Hz), 132.5 (d, J_{C-P} = 9.8 Hz), 130.4 (d, J_{C-P} = 7.9 Hz), 130.3 (d, J_{C-P} = 100.0 Hz), 130.1 (d, J_{C-P} = 5.2 Hz), 129.0 (d, J_{C-P} = 12.2 Hz), 128.6 (d, J_{C-P} = 2.4 Hz), 127.1 (d, J_{C-P} = 2.9 Hz), 38.0 (d, J_{C-P} = 66.8 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 28.6. This compound is known.[21]

Di([1,1′-biphenyl]-4-yl)(benzyl)phosphine Oxide (3za). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 88% yield (78.2 mg), mp: 250.2−251.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.68 (m, 4H), 7.61−7.59 (m, 4H), 7.54−7.51 (m, 4H), 7.40−7.36 (m, 4H), 7.33−7.29 (m, 2H), 7.14−7.08 (m, 5H), 3.65 (d, J = 13.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.6 (d, J_{C-P} = 2.7 Hz), 139.8, 131.7 (d, J_{C-P} = 9.4 Hz), 131.1 (d, J_{C-P} = 7.9 Hz), 130.8 (d, J_{C-P} = 99.8 Hz), 130.2 (d, J_{C-P} = 5.2 Hz), 128.9, 128.4 (d, J_{C-P} = 2.4 Hz), 128.1, 127.2, 127.1, 126.8 (d, J_{C-P} = 2.8 Hz), 38.2 (d, J_{C-P} = 66.6 Hz). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 29.6. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{26}OP$, 445.1721; found, 445.1721.

Benzyl(butyl)(phenyl)phosphine Oxide (3zb). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 42% yield (22.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.48 (m, 2H), 7.45−7.41 (m, 1H), 7.38−

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7.34 (m, 2H), 7.20−7.13 (m, 3H), 7.02−7.00 (m, 2H), 3.30−3.18 (m, 2H), 1.95−1.74 (m, 2H), 1.59−1.48 (m, 1H), 1.38−1.21 (m, 3H), 0.77 (t, J_{C-P} = 7.2 Hz, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 131.8 (d, J_{C-P} = 7.4 Hz), 131.7 (d, J_{C-P} = 92.4 Hz), 131.5 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 8.6 Hz), 129.7 (d, J_{C-P} = 4.9 Hz), 128.5 (d, J_{C-P} = 2.6 Hz), 128.4 (d, J_{C-P} = 11.1 Hz), 126.7 (d, J_{C-P} = 3.0 Hz), 38.9 (d, J_{C-P} = 61.9 Hz), 27.9 (d, J_{C-P} = 69.0 Hz), 24.0 (d, J_{C-P} = 14.5 Hz), 23.2 (d, J_{C-P} = 4.2 Hz), 13.5. ^{31}P {^1H} NMR (162 MHz, $CDCl_3$): δ 38.2. This compound is known.[81]

Benzyldibutylphosphine Oxide (3zc). The title compound was prepared according to the general experimental procedure I, purified by column chromatography on silica gel, and eluted with EA: DCM = 10:1 (v/v) to afford a white solid in 50% yield (25.2 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.30 (m, 2H), 7.27−7.23 (m, 3H), 3.13 (d, J = 14.4 Hz, 2H), 1.66−1.52 (m, 8H), 1.43−1.34 (m, 4H), 0.96−0.89 (m, 6H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 132.4 (d, J_{C-P} = 6.9 Hz), 129.4 (d, J_{C-P} = 5.0 Hz), 128.8 (d, J_{C-P} = 2.5 Hz), 126.8 (d, J_{C-P} = 2.9 Hz), 36.3 (d, J_{C-P} = 58.6 Hz), 27.0 (d, J_{C-P} = 65.5 Hz), 24.2 (d, J_{C-P} = 14.3 Hz), 23.6 (d, J_{C-P} = 4.0 Hz), 13.5. ^{31}P {^1H} NMR (162 MHz, $CDCl_3$): δ 46.7. This compound is known.[22]

(Benzyloxy)benzene (5a). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 74% yield (27.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.28 (m, 4H), 7.26−7.18 (m, 3H), 6.91−6.86 (m, 3H), 4.98 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 158.7, 137.0, 129.4, 128.5, 127.9, 127.4, 120.9, 114.8, 69.9. This compound is known.[23]

1-(Benzyloxy)-4-methoxybenzene (5b). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a white solid in 75% yield (32.1 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.41 (m, 2H), 7.39−7.36 (m, 2H), 7.33−7.29 (m, 1H), 6.92−6.90 (m, 2H), 6.84−6.81 (m, 2H), 5.00 (s, 2H), 3.76 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 153.9, 152.9, 137.3, 128.5, 127.8, 127.4, 115.8, 114.6, 70.7, 55.7. This compound is known.[23]

(4-(Benzyloxy)phenyl)(methyl)sulfane (5c). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a white solid in 92% yield (42.4 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41−7.34 (m, 4H), 7.32−7.29 (m, 1H), 7.25−7.21 (m, 2H), 6.91−6.89 (m, 2H), 5.02 (s, 2H), 2.42 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 157.2, 136.8, 129.9, 129.1, 128.5, 127.9, 127.4, 115.5, 70.0, 17.8. This compound is known.[24]

1-(Benzyloxy)-4-(*tert*-butyl)benzene (5d). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 78% yield (37.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.36−7.28 (m, 4H), 7.25−7.21 (m, 3H), 6.84 (d, J = 8.4 Hz, 2H), 4.96 (s, 2H), 1.22 (s, 9H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 156.6, 143.6, 137.3, 128.5, 127.8, 127.5, 126.2, 114.2, 70.0, 34.1, 31.5. This compound is known.[23]

2-(Benzyloxy)-1,1′-biphenyl (5e). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 94% yield (48.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.48 (m, 2H), 7.31−7.24 (m, 3H), 7.23−7.13 (m, 7H), 6.95−6.89 (m, 2H), 4.95 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 155.5, 138.5, 137.2, 131.3, 130.9, 129.6, 128.5, 128.4, 127.9, 127.5, 126.9, 126.8, 121.3, 113.3, 70.4. This compound is known.[25]

1-(Benzyloxy)-4-fluorobenzene (5f). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 50:1 (v/v) to afford a white solid in 71% yield (28.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.27 (m, 4H), 7.26−7.21 (m, 1H), 6.91−6.85 (m, 2H), 6.84−6.79 (m, 2H), 4.93 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 157.3 (C−F, $^1J_{C-F}$ = 236.9 Hz), 154.8 (C−F, $^3J_{C-F}$ = 2.0 Hz), 136.81, 128.58, 128.01, 127.44, 115.9 (C−F, $^3J_{C-F}$ = 2.0 Hz), 115.7 (C−F, $^2J_{C-F}$ = 13.1 Hz), 70.6. This compound is known.[26]

1-(Benzyloxy)-4-chlorobenzene (5g). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 50:1 (v/v) to afford a white solid in 68% yield (29.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.33−7.27 (m, 4H), 7.25−7.22 (m, 1H), 7.15−7.12 (m, 2H), 6.81−6.79 (m, 2H), 4.93 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 157.3, 136.5, 129.3, 128.6, 128.1, 127.4, 125.8, 116.1, 70.2. This compound is known.[23]

1-(Benzyloxy)-4-bromobenzene (5h). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 57% yield (30.0 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.42−7.31 (m, 7H), 6.86−6.82 (m, 2H), 5.02 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 157.8, 136.5, 132.3, 128.6, 128.1, 127.4, 116.7, 113.1, 70.2. This compound is known.[23]

1-(Benzyloxy)-4-iodobenzene (5i). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 53% yield (32.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55−7.53 (m, 2H), 7.39−7.30 (m, 5H), 6.76−6.72 (m, 2H), 5.01 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 158.6, 138.2, 136.4, 128.6, 128.1, 127.4, 117.2, 83.0, 70.0. This compound is known.[23]

1-(Benzyloxy)-4-(trifluoromethoxy)benzene (5j). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 77% yield (41.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.43−7.37 (m, 4H), 7.35−7.32 (m, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.97−6.93 (m, 2H), 5.04 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 157.2, 142.9, 142.8, 136.5, 128.6, 128.1, 127.4, 122.4, 120.5 (q, J_{C-F} = 254.5 Hz), 115.6, 70.4. This compound is known.[27]

1-(3-(Benzyloxy)phenyl)ethan-1-one (5k). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 10:1 (v/v) to afford a colorless oil in 55% yield (24.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51−7.50 (m, 1H), 7.49−7.46 (m, 1H), 7.38−7.36 (m, 2H), 7.34−7.24 (m, 4H), 7.12−7.09 (m, 1H), 5.03 (s, 2H), 2.51 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 197.9, 158.9, 138.5, 136.5, 129.6, 128.6, 128.1, 127.5, 121.3, 120.3, 113.5, 70.1, 26.7. This compound is known.[28]

Ethyl 4-(benzyloxy)benzoate (5l). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a white solid in 60% yield (30.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.8 Hz, 2H), 7.43−7.30 (m, 5H), 6.99−6.96 (m, 2H), 5.09 (s, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H), 2.51 (s, 3H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 166.3, 162.3, 136.2, 131.5, 128.6, 128.1, 127.4, 123.1, 114.3, 70.0, 60.6, 14.3. This compound is known.[29]

2-(Benzyloxy)naphthalene (5m). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 75% yield (35.1 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.63 (m, 3H), 7.42−7.40 (m, 2H), 7.37−7.30 (m, 3H), 7.27−7.23 (m, 2H), 7.16−7.14 (m, 2H), 5.09 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 156.7, 136.9, 134.5, 129.4, 129.0, 128.6, 128.0, 127.6, 127.6, 126.8, 126.3, 123.7, 119.0, 107.1, 70.0. This compound is known.[23]

1-(Benzyloxy)naphthalene (5n). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 78% yield (36.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.27−8.24 (m, 1H), 7.71−7.68 (m, 1H), 7.43−7.22 (m, 9H), 6.76 (d, J = 7.6 Hz, 1H), 5.12 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 154.4, 137.1, 134.5, 128.5, 127.9, 127.4, 127.3, 126.4, 125.8, 125.7, 125.2, 122.2, 120.4, 105.1, 70.0. This compound is known.[29]

1-(Benzyloxy)-4-methoxynaphthalene (5o). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a colorless oil in 88% yield (46.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.23−8.19 (m, 1H), 8.15−8.11 (m, 1H),

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7.42−7.38 (m, 4H), 7.32−7.27 (m, 2H), 7.25−7.21 (m, 1H), 6.65−6.63 (m, 2H), 5.07 (s, 2H), 3.82 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.6, 148.5, 137.4, 128.5, 128.5, 127.8, 127.3, 126.5, 126.3, 125.9, 125.8, 121.9, 121.7, 104.9, 103.1, 70.4, 55.6. This compound is known.[30]

1-(Benzyloxy)-4-chloronaphthalene (5p). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 60% yield (32.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29−8.26 (m, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.54−7.50 (m, 1H), 7.46−7.39 (m, 3H), 7.35−7.30 (m, 3H), 7.28−7.24 (m, 1H), 6.68 (d, J = 8.4 Hz, 1H), 5.12 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.5, 136.7, 131.3, 128.6, 128.0, 127.5, 127.3, 126.7, 126.0, 125.7, 124.2, 123.4, 122.6, 105.2, 70.3. This compound is known.[31]

(Oxybis(methylene))dibenzene (5q). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 25:1 (v/v) to afford a colorless oil in 52% yield (20.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.31 (m, 8H), 7.28−7.24 (m, 2H), 4.53 (s, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 128.3, 127.7, 127.5, 72.0. This compound is known.[32]

2-((Benzyloxy)methyl)furan (5r). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 15:1 (v/v) to afford a colorless oil in 47% yield (17.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.40 (m, 1H), 7.36−7.33 (m, 4H), 7.29−7.25 (m, 1H), 6.34−6.31 (m, 2H), 4.54 (s, 2H), 4.48 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.7, 142.8, 137.8, 128.3, 127.8, 127.6, 110.2, 109.3, 71.8, 63.8. This compound is known.[33]

(((4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)methoxy)methyl)-benzene (5s). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a colorless oil in 40% yield (19.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.31 (m, 4H), 7.28−7.24 (m, 1H), 5.73−5.72 (m, 1H), 4.73−4.71 (m, 2H), 4.56 (s, 2H), 3.89 (s, 2H), 2.18−2.09 (m, 4H), 2.02−1.93 (m, 1H), 1.88−1.82 (m, 1H), 1.74 (s, 3H), 1.54−1.43 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.8, 138.6, 134.6, 128.3, 127.7, 127.4, 124.6, 108.6, 74.5, 71.6, 41.1, 30.5, 27.4, 26.4, 20.7. This compound is known.[34]

Benzyl(*p*-tolyl)sulfane (6a). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a white solid in 80% yield (34.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20−7.17 (m, 4H), 7.15−7.10 (m, 3H), 6.96 (s, J = 8.0 Hz, 2H), 3.97 (s, 2H), 2.21 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.7, 136.5, 132.4, 130.6, 129.5, 128.8, 128.4, 127.0, 39.7, 21.0. This compound is known.[12a]

Benzyl(4-(*tert*-butyl)phenyl)sulfane (6b). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 85% yield (43.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.12 (m, 9H), 4.01 (s, 2H), 1.21 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.6, 137.7, 132.9, 129.8, 128.8, 128.4, 127.1, 125.8, 39.4, 34.4, 31.2. This compound is known.[12a]

Benzyl(4-chlorophenyl)sulfane (6c). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 50:1 (v/v) to afford a white solid in 74% yield (34.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23−7.15 (m, 5H), 7.12 (s, 4H), 3.99 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.1, 134.6, 132.4, 131.4, 128.9, 128.7, 128.5, 127.3, 39.2. This compound is known.[12a]

Benzyl(4-bromophenyl)sulfane (6d). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 50:1 (v/v) to afford a white solid in 76% yield (42.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.25 (m, 2H), 7.22−7.13 (m, 5H), 7.07−7.04 (m, 2H), 3.99 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.0, 135.4, 131.8, 131.4, 128.7, 128.5, 127.3, 120.2, 39.0. This compound is known.[12a]

Benzyl(4-(trifluoromethyl)phenyl)sulfane (6e). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 30:1 (v/v) to afford a white solid in 78% yield (41.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2H), 7.27−7.16 (m, 7H), 4.10 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.03, 142.02, 136.3, 128.71, 128.67, 127.9, 127.5, 125.6 (C−F, $^{2}J_{C-F}$ = 3.8 Hz), 124.1 (C−F, $^{1}J_{C-F}$ = 270.1 Hz), 37.6. This compound is known.[35]

Benzyl(naphthalen-2-yl)sulfane (6f). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 30:1 (v/v) to afford a white solid in 91% yield (45.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.67 (m, 1H), 7.64−7.59 (m, 3H), 7.38−7.30 (m, 3H), 7.25−7.12 (m, 5H), 4.12 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.3, 133.9, 133.7, 131.8, 128.8, 128.5, 128.3, 127.6, 127.6, 127.2, 127.1, 126.4, 125.7, 38.8. This compound is known.[12a]

2-(Benzylthio)thiophene (6g). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 30:1 (v/v) to afford a colorless oil in 73% yield (30.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22−7.21 (m, 1H), 7.20−7.14 (m, 3H), 7.08−7.05 (m, 2H), 6.85−6.80 (m, 2H), 3.87 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.6, 134.3, 133.5, 129.7, 128.9, 128.3, 127.4, 127.2, 43.8. This compound is known.[36]

Benzyl(cyclohexyl)sulfane (6h). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 60% yield (24.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.20 (m, 4H), 7.16−7.12 (m, 1H), 3.66 (s, 2H), 2.51−2.44 (m, 1H), 1.88−1.85 (m, 2H), 1.68−1.64 (m, 2H), 1.51−1.49 (m, 1H), 1.30−1.13 (m, 5H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.89, 128.7, 128.4, 126.7, 42.8, 34.5, 33.3, 25.9, 25.8. This compound is known.[37]

Benzyl(hexyl)sulfane (6i). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE to afford a colorless oil in 65% yield (27.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.20 (m, 4H), 7.17−7.12 (m, 1H), 3.62 (s, 2H), 2.32 (t, J = 7.6 Hz, 2H), 1.50−1.43 (m, 2H), 1.28−1.14 (m, 6H), 0.80 (t, J = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.6, 128.8, 128.4, 126.8, 36.2, 31.4, 31.3, 29.1, 28.5, 22.5, 14.0. This compound is known.[37]

1-Benzyl-5-methoxy-1*H*-indole (7a). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a colorless oil in 60% yield (28.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.21 (m, 3H), 7.17−7.09 (m, 2H), 7.06−7.04 (m, 3H), 6.82−6.80 (m, 1H), 6.45 (d, J = 2.8 Hz, 1H), 5.22 (s, 2H), 3.81 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.0, 137.6, 131.5, 129.0, 128.8, 128.7, 127.5, 126.6, 111.9, 110.4, 102.5, 101.1, 55.7, 50.2. This compound is known.[12b]

1-Benzyl-5-chloro-1*H*-indole (7b). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a colorless oil in 68% yield (32.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 2.0 Hz, 1H), 7.27−7.21 (m, 3H), 7.12−7.05 (m, 3H), 7.03−7.01 (m, 2H), 6.44 (d, J = 3.2 Hz, 1H), 5.20 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.0, 134.6, 129.7, 129.6, 128.7, 127.7, 126.6, 125.2, 121.9, 120.3, 110.7, 101.3, 50.2. This compound is known.[38]

1-Benzyl-1*H*-indole-5-carbonitrile (7c). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 10:1 (v/v) to afford a white solid in 57% yield (26.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 0.8 Hz, 1H), 7.37−7.34 (m, 1H), 7.32−7.27 (m, 4H), 7.24 (d, J = 3.2 Hz, 1H), 7.09−7.07 (m, 2H), 6.61−6.60 (m, 1H), 5.32 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.7, 136.3, 130.5, 128.9, 128.3, 128.0, 126.6, 126.5, 124.5, 120.7, 110.5, 102.7, 102.5, 50.3. This compound is known.[38]

10-Benzyl-10*H*-phenothiazine (7d). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 50:1 (v/v) to afford a pale yellow solid in 59% yield (34.1 mg). ^{1}H NMR

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(400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 4H), 7.24−7.21 (m, 1H), 7.07−7.05 (m, 2H), 6.96−6.92 (m, 2H), 6.85−6.81 (m, 2H), 6.61 (d, J = 8.0 Hz, 2H), 5.05 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 144.4, 136.6, 128.7, 127.2, 126.9, 126.8, 126.5, 123.0, 122.4, 115.4, 52.6. This compound is known.[39]

9-Benzyl-9*H*-carbazole (7e). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a white solid in 57% yield (29.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 7.6 Hz, 2H), 7.43−7.42 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.26−7.21 (m, 5H), 7.13−7.11 (m, 2H), 5.49 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 140.6, 137.1, 128.7, 127.4, 126.4, 125.8, 123.0, 120.4, 119.2, 108.9, 46.5. This compound is known.[12b]

1-Benzyl-1*H*-benzo[*d*]imidazole (7f). The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 1:1 (v/v) to afford a white solid in 48% yield (20.0 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.84−7.82 (m, 1H), 7.35−7.24 (m, 6H), 7.19−7.17 (m, 2H), 5.35 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 135.4, 133.9, 129.0, 128.2, 127.0, 123.0, 122.2, 120.4, 110.0, 48.8. This compound is known.[12b]

***N*-Benzyl-*N*-phenylaniline (7g).** The title compound was prepared according to the general experimental procedure II, purified by column chromatography on silica gel, and eluted with PE/EA = 20:1 (v/v) to afford a colorless oil in 63% yield (32.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.33 (m, 2H), 7.30−7.27 (m, 2H), 7.25−7.20 (m, 5H), 7.07−7.04 (m, 4H), 6.94−6.90 (m, 2H), 4.99 (s, 2H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 148.0, 139.1, 129.2, 128.5, 126.7, 126.5, 121.3, 120.6, 56.3. This compound is known.[40]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02992.

Copies of ^1H, ^{13}C, and ^{31}P NMR spectroscopies. (PDF)

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Notes

The authors declare no competing financial interest.

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