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RESEARCH ARTICLE

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2-(Arylamino)aryliminophosphoranes from 2-nitrodiarylamines

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Abstract

Deoxygenation of 2-nitrodiarylamines by triphenylphosphine is presented as an efficient method for synthesis of 2-(arylamino)aryliminophosphoranes, useful as starting materials in the synthesis of benzannulated nitrogen heterocycles. The reaction is complementary for the known synthesis of aryliminophosphoranes from 2-nitrosodiarylamines giving rise to obtain the title products in the broader scope. The presented protocol is simple and efficient although limited to secondary 2-nitrodiarylamines.

1 | INTRODUCTION

Aryliminophosphoranes, ylide-like species, exhibit reactivity which can be employed for the construction of different nitrogen functions. Suitable *ortho*-substituents in the aromatic ring allow cyclization reactions giving rise to the synthesis of various fused heterocyclic systems. In 2014, we described the efficient formation of 2-(arylamino)iminophosphoranes in the reaction of 2-nitrosodiarylamines with triphenylphosphine.[1] Due to the vicinity of the two different nitrogen functions, they turned out to be versatile equivalents for *o*-arylenediamines in the synthesis of a variety of nitrogen heterocycles like benzimidazoles,[1,2] triazoles,[3] benzimidazol-2-ones,[4] benzimidazol-2-thiones,[5] benzazepines.[2]

The proposed synthesis of 2-(arylamino)aryliminophosphoranes from 2-nitrosodiarylamines is high yielding and quite general reaction showing great tolerance toward various substituents in the starting nitrosanilines. The major problem in broadening its synthetic scope is availability of starting materials. Numerous of 2-nitrosodiarylamines can be easily obtained by nucleophilic substitution of hydrogen ($S_N{}^HAr$) in nitroarenes with arylamines in the presence of a strong base at low temperature.[6] However, certain types of them could not be obtained that way. For example, several heteroaromatic amines appeared unreactive due to low nucleophilicity of their stabilized anions, some nitroarenes with strong electron-withdrawing groups have a tendency to the oxidative substitution of hydrogen resulting in 2-nitroanilines, while strongly electron-donating substituents reduce electrophilic reactivity of the nitroarene giving rise to undesired processes when the temperature is increased (several 5-amino- and 5-alkoxy-substituted nitrosoanilines could be obtained by nucleophilic substitution of halogens in easily synthesized fluoro- or chloronitrosoanilines. See ref. [7]). Unfortunately, there are no other methods for the synthesis of 2-nitrosodiarylamines at the moment which could be considered as general and practical.

However, deoxygenation of an aromatic nitro group is known as an effective way to transform it into more reactive nitrogen functions of lower oxidation state, prone to undergo intramolecular reactions accomplishing heteroannulation of the starting system. The so called reductive cyclization can be performed by means of various reducing agents, and is a valuable method providing a variety of fused nitrogen heterocyclic systems.[8,9] A prominent class of deoxygenating agents of practical value are trivalent phosphorous compounds, such as trialkyl and triaryl phosphines and trialkyl phosphites.[10] Removing oxygen atoms from the nitro group is believed, according to the commonly supposed mechanism, to proceed stepwise through a formation of a nitroso group and a nitrene function.[11,12] In some reported cases, however, deoxygenation of the intermediate nitrosoarene leads to the formation of phosphorimidate or iminophosphorane function instead of the desired cyclization products.[13–16] This appears as a result of reactions of the intermediate nitrenes with highly nucleophilic trialkyl phosphite or phosphine, respectively. The deoxygenation of nitroarenes has never become a practical method for the

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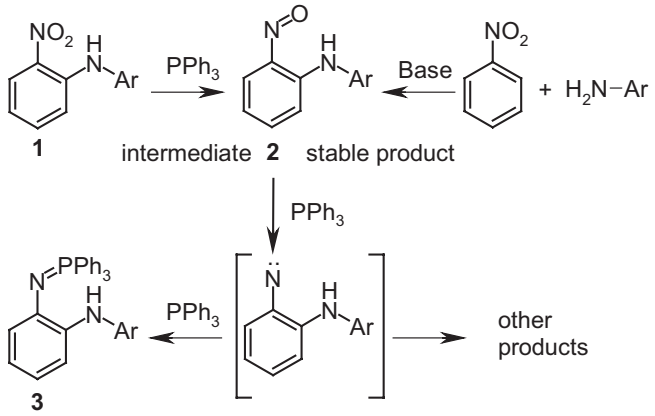


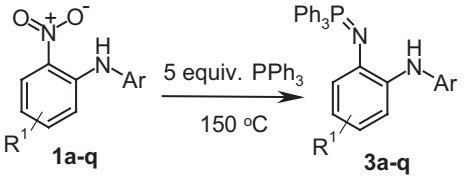
SCHEME 1 General reaction of 2-nitroso and 2-nitrodiarylamines with triphenylphosphine

synthesis of aryliminophosphoranes because of its unpredictability and because other, much more general methods, such as the Staudinger reaction,[17] have been developed. Deoxygenation of nitroarenes having *o*-amine group by trivalent phosphorus compounds has been reported to give varied results, providing phosphorimidates,[15] dihydrophenazine derivatives,[18] or phenazine.[19]

Examples of isolated aryliminophosphoranes obtained that way from *o*-aminonitroarene derivatives are rare,[14,16] being rather exceptions from the major reaction course. Nevertheless, the reaction attracted our attention as a potential alternative to the method of synthesis of 2-(arylamino) aryliminophosphoranes, which we have developed lately. Thus, our goal was to make use of the deoxygenation of the nitro group in 2-arylaminonitroarenes to generate 2-nitrosodiarylamines as intermediates, subsequently trapped with an excess of triphenylphosphine (Scheme 1). We expected that such procedure would considerably broaden the scope of available 2-(arylamino)aryliminophosphoranes and increase their value as starting materials in the synthesis of nitrogen heterocyclic systems.

2 | RESULTS AND DISCUSSION

While 2-nitrosodiarylamines react with PPh_3 quickly at ambient temperature, deoxyganation of nitroarenes is known to require much higher temperature. To avoid possible side reactions of the intermediate nitrene under harsh conditions, the use of a reasonable excess of triphenylphosphine seemed to be necessary. The preliminary experiments proved those predictions. However, the reaction of 4-chloro-2-nitro-4′-methoxydiarylamine with 5 equiv. of PPh_3 carried out in various solvents at temperature up to 150°C gave rather poor results. Satisfactory effect was finally obtained in the reaction carried out without a solvent in a melted mixture of the nitroarene and 5 equiv. of PPh_3 at 150°C.[20] After



SCHEME 2 Formation of aryliminophosphoranes from 2-nitrodiarylamines in selected conditions

stirring the mixture for 12 h followed by column chromatography, iminophosphorane 3a was isolated in 86% yield. Under such reaction conditions, further nitroanilines were successfully transformed into products shown in Scheme 2 and Table 1.[21]

Despite rather harsh reaction conditions, the reaction proceeded well, providing desired iminophosphoranes in moderate to excellent yields. Regarding the already known iminophosphoranes **3a–c**, the yields obtained in the direct reaction of the corresponding nitrosoanilines **2** were higher, although.[1,3,4] The important procedure is, however, that according to our expectations, it opens the possibility to obtain 2-(arylamino)aryliminophosphoranes which are unavailable from the direct reactions of corresponding 2-nitrosoanilines when the latter are difficult or impossible to obtain by the methods described previously.[6,7]

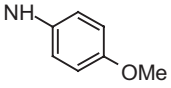
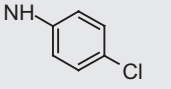
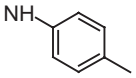
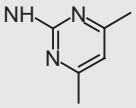
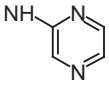
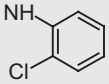
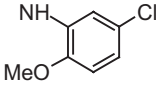
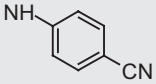
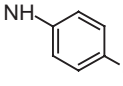
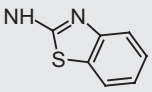
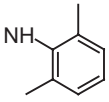
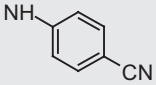
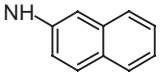
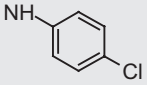
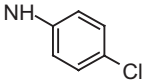
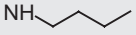
Among these are, for instance, derivatives of heterocyclic amines **3d**, **3e**, and **3j**, dicyano compound **3l**, as well as **3k**, derived from poorly electrophilic *p*-morpholinonitrobenzene. In addition, it was difficult to obtain 2-nitrosoanilines from the reaction of nitroarenes with 2-naphtylamine because of fast cyclization of the desired product under the reaction conditions affording 5,10-diazatetraphene derivative.

Thus, formation of **3m** from the corresponding 2-nitroaniline also demonstrates the advantage of this approach.

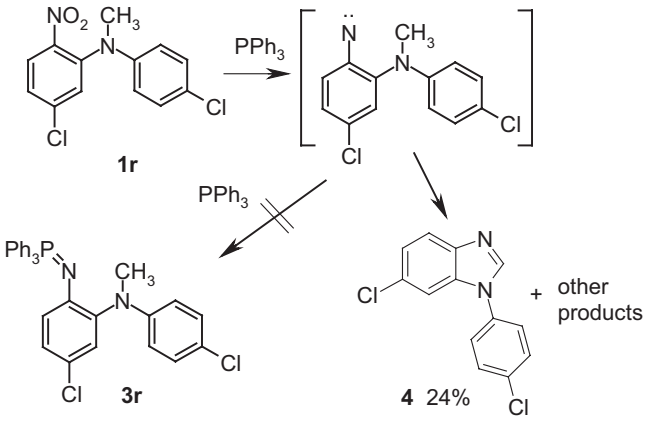
Starting *o*-arylaminonitroarenes **1** were obtained by standard nucleophilic substitution of *o*-fluorine or other halogens with suitable arylamine, although the reactions required harsh conditions, long time and also catalysts sometime to proceed (see Section 4).

Despite of the quite broad range of the obtained yields, the reaction can be regarded as general, at least taking into considerations secondary 2-nitrodiarylamines. It was, however, of interest to obtain that way aryliminophosphoranes with *N*-alkylarylamine group at *o*-position because *N*-alkylated 2-nitrosodiarylamines which could be a starting material for the reaction with triphenylphosphine, have not been obtained until now. Unfortunately, the attempted reaction of *N*-methyl-4′,5-dichloro-2-nitroaniline under regular reaction conditions did not afford desired iminophosphorane. Instead, benzimidazole **4** was formed in 24% yield as only isolable product (Scheme 3). Stability of **3r** under the reaction conditions should not differ from that

TABLE 1 Iminophosphoranes **3** obtained from nitroarenes **1** (Scheme 2)

Entry	R^1	NH-Ar	3a–q	Yield[a] %
1	4-Cl		**3a**	86
2	5-CF_3		**3b**	77
3	4-Cl		**3c**	86
4	H		**3d**	67
5	4-Cl		**3e**	71
6	H		**3f**	63
7	5-CF_3		**3g**	97
8	4-Cl		**3h**	82
9	5-Cl		**3i**	46
10	H		**3j**	67
11	4- 		**3k**	28
12	4-CN		**3l**	76
13	4-Cl		**3m**	51
14	5-Me		**3n**	56
15	5-OMe		**3o**	27
16	4-Cl		**3p**	27
17	4-Cl		**3q**	79

[a]Isolated yield.



SCHEME 3 Reaction of N-methyl-(5,4'-dichloro-2-nitro) diphenylamine with triphenylphosphine

of the unsubstituted products **3**, thus, it seems reasonable to assume that iminophosphorane **3r** was not formed in the reaction. Apparently, reduction of the intermediate nitroso compound led to the nitrene **5** followed by its insertion to the CH bond of the *N*-methyl group.

The nitrene intermediate did also undergo other side reactions, as the yield of **4** was low. Thus, the question arises, why the capture of the nitrene by triphenylphosphine is so ineffective in this case.

There are a few known issues concerning *N*-substituted versus unsubstituted nitroanilines in the reported reactions of the deoxygenation of nitroarenes by trivalent phosphorus compounds. In the reaction of triphenylphosphine with *o*-nitroanilides developed by Vasella et al. 2-alkylbenzimidazoles were obtained via subsequent formation of nitrene, imiophosphorane, and its aza-Wittig cyclization with the carbonyl group.[16] *N*-Alkylated *o*-nitroanilides, however, behaved differently, the nitrene added to the amide oxygen atom followed by electrocyclization and some further rearrangements leading to benzimidazolones. The authors tried to explain these results considering a function of hydrogen bond between both nitrogen atoms in the critical intermediates and implications of its absence. Quite different reaction course of triethyl phosphite with *N*-aryl-2-nitroacetanilide derivative has been reported by Maki et al.[18] *N*-Arylbenzimidazole, formed via the aza-Wittig cyclization of the triethyl phosphorimidate, was isolated in 3% yield, while the main product was *N*-acyldihydrophenazine, formed by intramolecular, multistep reaction of the intermediate nitrene with the aryl ring. As it was reported, the reaction of similar, although unacylated *N*-aryl-2-nitroaniline was complicated, and no defined product was isolated.[18] However, *N*-phenyl-2-nitroaniline was reported to cyclize efficiently to afford phenazine when reacted with PPh_3 or $(EtO)_3P$ under microwave conditions.[19] Unfortunately, all those reports did not put any light on the results described here.

3 | CONCLUSION

In summary, the deoxygenation of aromatic nitroarenes by triphenylphosphine has been adopted to the efficient synthesis of 2-(arylamino)aryliminophosphoranes, useful starting materials in the synthesis of benzannulated nitrogen heterocycles. The reaction is simple, it utilizes obtainable 2-nitrodiarylamines and constitutes a complementary protocol for the synthesis of corresponding aminophosphoranes from 2-nitrosodiarylamines.

4 | EXPERIMENTAL

4.1 | General remarks

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian-NMR-vnmrs600 and a Varian Mercury 500 instruments, all at 298 K. Chemical shifts are expressed in ppm referred to TMS. Coupling constants are expressed in Hertz. Mass spectra (EI, 70 eV and ESI) were obtained using an AutoSpec Premier (Waters) spectrometer (EI, 70 eV) and API 365i spectrometers (ESI in MeOH). IR spectra were recorded on a FT/IR Jasco 6200 spectrometer in KBr. Silica gel Merck 60 (230–400 mesh) was used for column chromatography. DMF was dried over CaH_2, distilled and stored over molecular sieves.

Procedures for the synthesis of 2-nitrodiarylamines **1** were not optimized. The starting nitroarenes and arylamines were commercially available.

4.2 | Synthesis of 2-nitrodiarylamines 1

4.2.1 | *N*-(5-Chloro-2-nitrophenyl)-*N*-(4-methoxyphenyl)amine (1a)

Compound **1a** was obtained according to the known procedure.[20] NMR spectra in accord with those described earlier.[20]

4.2.2 | *N*-(4-Chlorophenyl)-*N*-[2-nitro-4-(trifluoromethyl)phenyl]amine (1b)

Compound **1b** was obtained according to the known procedure.[21] Orange solid; IR (KBr): ν = 3350, 3104, 1901, 1828, 1641, 1574, 1493, 1328, 1254, 1150. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.20 (m, 1 H), 7.22–7.27 (m, 2 H), 7.42–7.46 (m, 2 H), 7.54–7.58 (m, 1 H), 8.51 (s, 1 H), 9.63 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.4, 119.8 (d, J_{CF} = 34 Hz), 123.3 (d, J_{CF} = 270 Hz), 124.8 (q, J_{CF} = 4 Hz), 126.4, 130.2, 131.8 (d, J_{CF} = 4 Hz), 132.1, 132.4, 136.1, 144.9. MS (EI) *m/z* (%) = 318 (44), 317 (26), 316 [M^+] (100), 297 (14), 282 (30), 269 (44), 235 (42), 201 (17). HRMS (EI): Calcd for $C_{13}H_8N_2O_2{}^{35}ClF_3$: 316.0226, found: 316.0224.

4.2.3 | *N*-(5-Chloro-2-nitrophenyl)-*N*-(4-methylphenyl)amine (1c)

Compound **1c** was obtained according to the known procedure.[22] Red solid; IR (KBr): ν = 3332, 1605, 1564, 1511, 1483, 1314, 1245. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 6.69 (dd, J = 9.0, 2.1 Hz, 1 H), 7.07 (d, J = 2.1 Hz, 1 H), 7.14–7.17 (m, 2 H), 7.24–7.27 (m, 2 H), 8.17 (d, J = 9.0 Hz, 1 H), 9.49 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0, 115.1, 117.5, 125.2, 128.1, 130.6, 131.2, 135.1, 136.5, 142.4, 144.5. MS (EI) *m/z* (%) = 264 (49), 262 [M^+] (100), 245 (12), 228 (44), 215 (39), 180 (38), 152 (12); HRMS (EI): Calcd for $C_{13}H_{11}N_2O_2{}^{35}Cl$: 262.0509; found: 262.0507.

4.2.4 | 4,6-Dimethyl-*N*-(2-nitrophenyl) pyrimidin-2-amine (1d)

2-Iodonitrobenzene (2.49 g, 10 mmol), 4,6-dimethylpyrimidin-2-amine (1.23 g, 10 mmol), CuI (1.9 g, 10 mmol), and powdered K_2CO_3 (3.45 g, 25 mmol) were stirred in *N*-methylpyrrolidone (20 mL) at 110°C overnight. The reaction mixture was cooled to the room temperature, poured into diluted aqueous NaCl, and filtered. The filtrate was extracted with EtOAc, the extract was washed with water, and dried with Na_2SO_4. After evaporation, the residue was chromatographed (SiO_2, hexane/EtOAc). Yellow fine crystals, mp: 165–168°C; yield: 0.61 g (25%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 6 H), 6.68 (s, 1 H), 7.02–7.06 (m, 1 H), 7.62–7.66 (m, 1 H), 8.24–8.27 (m, 1 H), 9.11–9.14 (m, 1 H), 10.40 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.9, 113.7, 120.3, 120.8, 126.0, 135.3, 137.6, 159.0, 167.8, one signal invisible. MS (EI) *m/z* (%) = 244 [M^+] (14), 199 (24), 198 (100), 197 (20), 118 (4); HRMS (EI): Calcd for $C_{12}H_{12}N_4O_2$: 244.0960; found: 244.0962.

4.2.5 | *N*-(5-Chloro-2-nitrophenyl)pyrazin-2-amine (1e)

2,4-dichloronitrobenzene (1.92 g, 10 mmol), pyrazin-2-amine (0.95 g, 10 mmol), and K_2CO_3 (3.45 g, 25 mmol) were stirred in *N*-methylpyrrolidone (20 mL) at 120–140°C overnight. After cooling and standard aqueous work-up, the product was isolated by column chromatography (SiO_2, hexane/EtOAc). Orange crystals, mp: 97–100°C; Yield: 0.3 g (12%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00–7.08 (m, 1 H), 7.60–7.65 (m, 1 H), 8.14–8.40 (m, 4 H), 8.78–8.83 (m, 1 H), 10.32 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.0, 121.0, 126.5, 135.6, 135.9, 136.8, 137.5, 137.8, 141.4, 150.6. MS (ESI) *m/z* (%) = 217.07 [M+H]$^+$. HRMS (ESI): Calcd for $C_{10}H_9N_4O_2$: 217.0726, found: 217.0726.

4.2.6 | *N*-(2-Chlorophenyl)-*N*-(2-nitrophenyl) amine (1f)

Compound **1f** was obtained according to the known procedure.[23] IR (KBr): $\nu = 3327$, 1617, 1582, 1510, 1262, 1148. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 6.83$–6.87 (m, 1 H), 7.14–7.19 (m, 2 H), 7.27–7.32 (m, 1 H), 7.39–7.43 (m, 1 H), 7.44–7.47 (m, 1 H), 7.50–7.52 (m, 1 H), 8.21–8.24 (m, 1 H), 9.47 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 116.2$, 118.4, 124.4, 126.1, 126.7, 127.5, 128.7, 130.6, 134.3, 135.6, 136.2, 141.5. MS (EI) *m/z* (%) = 250 (50), 248 (100) [M^+], 214 (33), 201 (54), 196 (47), 167 (68), 139 (28); HRMS (EI): Calcd for $C_{12}H_9N_2O_2{}^{35}Cl$: 248.0353; found: 248.0348.

4.2.7 | *N*-(5-Chloro-2-methoxyphenyl)-*N*-[2-nitro-4-(trifluoromethyl)phenyl]amine (1g)

1-Chloro-2-nitro-4-(trifluoromethyl)benzene(2.25 g,10 mmol), 5-chloro-2-methoxyaniline (1.89 g, 12 mmol), and anhydrous KF (2.9 g, 50 mmol) in *N*-methylpyrrolidone (20 mL) were stirred at 160–200°C overnight. After cooling and standard aqueous work-up, the product was isolated by column chromatography (SiO_2, hexane/EtOAc). Orange solid, mp: 138–143°C; yield: 0.88 g (30%); IR (KBr): $\nu = 3334$, 3080, 2943, 2841, 1830, 1637, 1596, 1534, 1491, 1271. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.87$ (s, 3 H), 6.94 (d, $J = 8.8$ Hz, 1 H), 7.20 (dd, $J = 8.8$, 2.5 Hz, 1 H), 7.26–7.29 (m, 1 H), 7.36 (d, $J = 2.5$ Hz, 1 H), 7.58–7.61 (m, 1 H), 8.50–8.52 (m, 1 H), 9.59 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 56.0$, 112.7, 116.7, 119.9 (q, $J_{CF} = 34$ Hz), 123.3 (q, $J_{CF} = 270$ Hz), 123.8, 124.7 (q, $J_{CF} = 4$ Hz), 125.6, 126.5, 127.7, 131.7 (q, $J_{CF} = 3$ Hz), 132.8, 143.9, 151.5. MS (EI) *m/z* (%) = 348 (49), 346 [M^+] (100), 299 (18), 285 (57), 262 (14), 222 (26); HRMS (EI): Calcd for $C_{14}H_{10}N_2O_3{}^{35}ClF_3$: 346.0332; found: 346.0323.

4.2.8 | 4-[(5-Chloro-2-nitrophenyl)amino] benzonitrile (1h)

Compound **1h** was obtained according to the known procedure.[24a] Orange crystals, mp: 243°C (ref. [24b]; mp 221–224°C); ^{1}H-NMR (500 MHz, DMSO-d_6): $\delta = 7.16$ (dd, $J = 2.1$, 8.8 Hz, 1 H); 7.4 (d, $J = 8.9$ Hz, 2 H); 7.78 (d, $J = 8.9$ Hz, 2 H); 7.45 (d, $J = 2.1$ Hz, 1 H); 8.14 (d, $J = 8.9$ Hz, 1 H); 9.48 (s, 1H). ^{13}C-NMR (125 MHz, DMSO-d_6): $\delta = 104.5$; 119.1; 119.2; 120.3; 121.1; 128.2; 133.7; 136.1; 139.1; 140.0; 144.8. MS (EI, 70 eV): 273 ($[M]^+$ (100), 256 (15), 239 (38), 228 (27). HRMS (EI): Calcd for $C_{13}H_8N_3O_2{}^{35}Cl$: 273.0305; found: 273.0304.

4.2.9 | *N*-(4-Chloro-2-nitrophenyl)-*N*-(4-chlorophenyl)amine (1i)

Compound **1i** was obtained according to the known procedure.[25] Orange solid; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.11$ (d, $J = 9.1$ Hz, 1 H), 7.18–7.22 (m, 2 H), 7.31–7.34 (dd, $J = 9.1$, 2.6 Hz, 1 H), 7.38–7.41 (m, 2 H), 8.21 (d, $J = 2.6$ Hz, 1 H), 9.35 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 117.3$, 122.6, 125.7, 125.9, 130.0, 131.4, 133.3, 135.9, 136.9, 141.4. MS (EI) *m/z* (%) = 286 (17), 284 (79), 282 [M^+] (100), 248 (39), 201 (68), 184 (27), 166 (23); HRMS (EI): Calcd for $C_{12}H_8N_2O_2{}^{35}Cl_2$: 281.9963; found: 281.9960.

4.2.10 | *N*-(2-Nitrophenyl)-1,3-benzothiazol-2-amine (1j)

Compound **1j** was obtained according to the known procedure.[26] Orange crystals, mp: 113–116°C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.11$–7.15 (m, 1 H), 7.27–7.30 (m, 1 H), 7.41–7.45 (m, 1 H), 7.70–7.75 (m, 2 H), 7.79–7.82 (m, 1 H), 8.27–8.30 (m, 1 H), 9.05–9.08 (m, 1 H), one signal invisible. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 120.6$, 120.9, 121.0, 121.8, 124.0, 126.2, 126.5, 130.6, 134.9, 136.4, 136.9, 151.1, 160.4. MS (EI) *m/z* (%) = 271 [M^+] (100), 254 (35), 225 (61), 224 (40), 148 (70); HRMS (EI): Calcd for $C_{13}H_9N_3O_2S$: 271.0415; found: 271.0418.

4.2.11 | *N*-(2,6-Dimethylphenyl)-*N*-(5-morpholin-4-yl-2-nitrophenyl)amine (1k)

2-[(2,6-Dimethylphenyl)amino]-4-fluoronitrobenzene (1.3 g, 5 mmol) and morpholine (1.7 g, 20 mmol) were stirred in MeCN (10 mL) at 100°C for 24 h. After the standard aqueous work-up, the product was purified by column chromatography (SiO_2, hexane/EtOAc). Yellow crystals, mp: 139–142°C; yield: 1.63 g (100%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.21$ (s, 3 H), 3.10–3.15 (m, 4 H), 3.70–3.75 (m, 4 H), 5.48–5.01 (m, 1 H), 6.24–6.28 (m, 1 H), 7.15–7.20 (m, 3 H), 8.12–8.16 (m, 1 H), 9.49 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.4$, 46.9, 66.4, 94.6, 104.7, 124.9, 127.6, 128.8, 128.9, 135.6, 136.6, 146.6, 156.2. MS (ESI) *m/z* (%) = 328.16 $[M+H]^+$, 350.15 $[M+Na]^+$, 677.31 $[2M+Na]^+$; HRMS (EI): Calcd for $C_{18}H_{21}N_3O_3Na$: 350.1481; found: 350.1485.

4.2.12 | 3-[(4-Cyanophenyl)amino]-4-nitrobenzonitrile (1l)

Compound **1l** was obtained as the only product in the attempted synthesis of the *N*-(4-cyanophenyl)-2-nitrosoaniline.[6] To a cooled solution of *t*-BuOK (6 mmol, 672 mg) in DMF (12 mL) was added dropwise at −60°C a solution of 4-cyanoaniline

(2 mmol), then 4-cyanonitrobenzene (2 mmol) in DMF (2 mL each). The mixture was stirred at this temperature for 5 min, the cooling bath was removed, and the mixture was allowed to reach the ambient temperature. It was then poured into diluted aqueous HCl (ca. 150 mL) and extracted with EtOAc The extract was washed with water, brine, and dried with Na_2SO_4. After evaporation, the crude product mixture was subjected to column chromatography (SiO2, hexane/EtOAc). Orange crystals, mp: 139–140°C; yield: 0.32 g (60%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.36–7.4 (m, 2 H), 7.53 (dd, J = 1.5, 8.5 Hz, 1 H), 7.75–7.79 (m, 2 H), 7.94 (d, J = 1.5 Hz, 1 H), 8.22 (d, J = 8.5 Hz, 1 H), 9.45 (s, 1 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 104.7, 117.6, 117.7, 119.6, 120.2, 124.5, 125.6, 127.8, 134.2, 138.1, 140.8, 145.5. MS (EI, 70 eV): m/z (%) = 264 (100), 247 (14), 230 (22), 219 (17). HRMS (EI): Calcd for $C_{14}H_8N_4O_2$: 264.0647; found: 264.0644.

4.2.13 | *N*-(5-Chloro-2-nitrophenyl)-*N*-2-naphthylamine (1m)

Compound **1m** was obtained according to the known procedure.[27] Orange fine crystals, mp: 103–106°C (ref. [27]; mp: 108–111°C); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.75 (dd, J = 9.1, 2.2 Hz, 1 H), 7.37–7.40 (m, 1 H), 7.49–7.56 (m, 2 H), 7.72–7.74 (m, 1 H), 7.21 (d, J = 2.2 Hz, 1 H), 7.80–7.89 (m, 2 H), 7.91–7.95 (m, 1 H), 8.19 (d, J = 9.1 Hz, 1 H), 9.69 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.3, 118.1, 122.3, 123.6, 126.1, 127.0, 127.5, 127.8, 128.1, 130.0, 131.7, 134.0, 135.3, 142.5, 143.9. MS (EI) m/z (%) = 300 (46), 299 (44), 298 [M^+] (100), 281 (33), 251 (40), 217 (53), 189 (30); HRMS (EI): Calcd for $C_{16}H_{11}N_2O_2{}^{35}Cl$: 298.0509; found: 298.0511.

4.2.14 | *N*-(4-Chlorophenyl)-*N*-(4-methyl-2-nitrophenyl)amine (1n)

Compound **1n** was obtained according to the known procedure.[28] Red crystals, mp: 84–87°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 7.10–7.13 (m, 1 H), 7.16–7.23 (m, 3 H), 7.33–7.37 (m, 2 H), 8.00 (br s, 1 H), 9.25 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 116.3, 125.1, 126.2, 128.1, 129.9, 130.3, 132.9, 137.2, 138.0, 140.5. MS (EI) m/z (%) = 264 (36), 263 (16), 262 [M^+] (100), 228 (22), 215 (25), 181 (30); HRMS (EI): Calcd for $C_{13}H_{11}N_2O_2{}^{35}Cl$:

4.2.15 | *N*-(4-Chlorophenyl)-*N*-(4-methoxy-2-nitrophenyl)amine (1o)

4-Methoxy-2-nitroaniline (3.74 g, 20 mmol), 4-bromochlorobenzene (4.79 g, 25 mmol), K_2CO_3 (4.10 g, 30 mmol), and Cu powder (0.64 g, 10 mmol) in isoamyl alcohol (10 mL) were stirred, boiled and the alcohol was gradually distilled off until the reaction started (tlc control). Then the reaction mixture was refluxed (ca. 200°C) for 2 h. After cooling down, the mixture was diluted with dichloromethane, filtered, and the solvent was evaporated. The crude product was chromatographed (SiO_2, hexane/EtOAc). Orange solid, mp: 98–101°C; yield: 2.09 g (38%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 7.09 (dd, J = 9.2, 3.0 Hz, 1 H), 7.15–7.18 (m, 2 H), 7.19 (d, J = 9.2 Hz, 1 H), 7.33–7.36 (m, 2 H), 7.64 (d, J = 3.0 Hz, 1 H), 9.21 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.9, 107.2, 117.9, 124.5, 126.0, 129.8, 130.0, 133.4, 137.2, 138.1, 151.6. MS (EI) m/z (%) = 280 (44), 279 (26), 278 (100), 244 (25), 231 (28), 216 (29), 197 (25), 182 (30), 154 (21); HRMS (EI): Calcd for $C_{13}H_{11}N_2O_3{}^{35}Cl$: 278.0458; found: 278.0460.

4.2.16 | *N*-Butyl-*N*-(5-chloro-2-nitrophenyl) amine (1p)

Compound **1p** was obtained according to the known procedure.[29a] Yellow crystals, mp: 27–29°C (ref. [29a]; oil, ref. [29b]; mp: 28°C) Yield: 171 mg (75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 3 H), 1.45–1.53 (m, 2 H), 1.69–1.76 (m, 2 H), 3.25–3.30 (m, 2 H), 6.59 (dd, J = 9.1, 2.0 Hz, 1 H), 6.83 (d, J = 2.0 Hz, 1 H), 8.05 (br s, 1 H), 8.11 (d, J = 9.1 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 20.2, 30.8, 42.9, 113.2, 115.6, 128.3, 130.2, 142.8, 145.9. MS (EI) m/z (%) = 230 (18), 228 [M^+] (37), 187 (42), 185 (100), 168 (10), 127 (31); HRMS (EI): Calcd for $C_{10}H_{13}N_2O_2{}^{35}Cl$: 228.0666; found: 228.0658.

4.2.17 | *N*-*tert*-Butyl-*N*-(5-chloro-2-nitrophenyl)amine (1q)

Compound **1q** was obtained according to the known procedure.[30] NMR spectra was in accordance with those described earlier.[30]

4.2.18 | *N*-(5-Chloro-2-nitrophenyl)-*N*-(4-chlorophenyl)-*N*-methylamine (1r)

To a solution of *N*-(5-chloro-2-nitrophenyl)-*N*-(4-chlorophenyl) amine[31] (2.83 g, 10 mmol) in DMF (30 mL) was added K_2CO_3 (35 mmol) and MeI (3 mL). The mixture was stirred at room temperature overnight, then it was poured into water and extracted with EtOAc. The extract was washed with water, dried with Na_2SO_4 and evaporated to obtain pure product. Orange oil; yield: 2.91 mg (98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.30 (s, 3 H), 6.69–6.73 (m, 2 H), 7.16–7.19 (m, 2 H), 7.21 (dd, J = 8.8, 2.2 Hz, 1 H), 7.33 (d, J = 2.2 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 40.8, 118.1, 124.8, 126.3, 127.3, 128.1, 129.3, 139.9, 143.2, 143.8, 145.9. MS (EI) m/z (%) = 300 (20), 298 (71), 296 (100), 279 (44), 263 (12), 251 (66), 249 (92), 214 (87), 164 (23); HRMS (EI): Calcd for $C_{13}H_{10}N_2O_2{}^{35}Cl_2$: 296.0119; found: 296.0128.

4.3 | Synthesis of 2-(arylamino) phenyliminophosphoranes 3 from 2-nitrodiarylamines 1

General procedure: To a solid 2-nitroaniline **1** (1 mmol) was added Ph_3P (5 mmol, 1310 mg), and the mixture was heated up to melt and stirred at 150°C for 2–12 h (tlc control). In the case of **3k**, 10 mmol of Ph_3P was used and the reaction was carried out at 220°C. After cooling down the crude mixture was chromatographed using hexane–EtOAc gradient elution (9:1–2:1). An analytically pure sample of **3** was obtained by recrystallization from EtOAc–hexane. In the reaction of **1q**, 6-chloro-1-(4-chlorophenyl)-1*H*-benzimidazole (**4**) was isolated instead of desired iminophosphorane.

2-(Arylamino)phenyliminophosphoranes **3a**,[3] **3b**,[4] **3c**,[1] **3g**,[4] and **3h**[3] have been described in our previous papers.

4.3.1 | 1-*N*-(4,6-dimethylpyrimidin-2-yl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3d)

Beige crystals, mp: 177–180°C; yield: 319 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6 H), 6.39–6.42 (m, 2 H), 6.49–6.53 (m, 1 H), 6.69–6.73 (m, 1H), 7.42–7.46 (m, 6 H), 7.49–7.54 (m, 3 H), 7.75–7.80 (m, 6 H), 8.55–8.58 (m, 1 H), 9.10 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 110.4, 117.0, 117.7, 119.3 (d, J_{CP} = 9 Hz), 120.5, 128.8 (d, J_{CP} = 12 Hz), 131.0 (d, J_{CP} = 99 Hz), 131.9 (d, J_{CP} = 3 Hz), 132.7 (d, J_{CP} = 10 Hz), 134.8 (d, J_{CP} = 20 Hz), 139.3, 160.5, 167.2. MS (EI) *m*/*z* (%) = 474 [M$^+$] (100), 473 (23). HRMS (EI): Calcd for $C_{30}H_{27}N_4P$: 474.1973; found: 474.1975.

4.3.2 | 1-*N*-(Pyrazin-2-yl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3e)

Beige crystals, mp: 167–170°C; yield: 317 mg, (71%).^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.47–6.50 (m, 1 H), 6.56–6.60 (m, 1 H), 7.45–7.50 (m, 6 H), 7.54–7.58 (m, 3 H), 6.71–6.76 (m, 1 H), 7.72–7.77 (m, 6 H), 7.83–7.85 (m, 1 H), 8.11 (br s, 1 H), 8.18 (br s, 1 H), 8.26–8.30 (m, 1 H), 8.80 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.4, 117.8, 119.4, 121.2, 128.8 (d, J_{CP} = 12 Hz), 130.5 (d, J_{CP} = 100 Hz), 131.9, 132.2, 132.5 (d, J_{CP} = 10 Hz), 133.0, 135.0, 139.4, 141.6, 152.5. MS (EI) *m*/*z* (%) = 446 [M$^+$] (100), 445 (43), 352 (13), 261 (42), 183 (50). HRMS (EI): Calcd for $C_{28}H_{23}N_4P$: 446.1660; found: 446.1664.

4.3.3 | 1-*N*-(2-Chlorophenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3f)

Yellow crystals, mp: 166–169°C; yield: 302 mg (63%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.51–6.53 (m, 2 H), 6.64–6.69 (m, 1 H), 6.71–6.75 (m, 1 H), 7.11–7.15 (m, 1 H), 7.33–7.36 (m, 2 H), 7.42–7.46 (m, 6 H), 7.50–7.54 (m, 4 H), 7.75–7.80 (m, 6 H), 8.02 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 114.8, 117.3, 118.9, 120.1, 120.2, 120.3, 121.9, 127.2, 128.6 (d, J_{CP} = 12 Hz), 129.5, 130.8 (d, J_{CP} = 99 Hz), 131.8, 132.6 (d, J_{CP} = 9 Hz), 136.0 (d, J_{CP} = 21 Hz), 140.3, 140.7. MS (EI) *m*/*z* (%) = 480 (49), 479 (49), 478 [M$^+$] (100), 443 (13), 262 (61), 181 (44). HRMS (EI): Calcd for $C_{30}H_{24}N_2P^{35}Cl$: 478.1366; found: 478.1367.

4.3.4 | 5-Chloro-1-*N*-(4-chlorophenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3i)

Beige crystals, mp: 143–146°C; yield: 235 mg, (46%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.35–6.37 (m, 1 H), 6.57–6.61 (m, 1 H), 7.06–7.10 (m, 3 H), 7.36–7.42 (m, 1 H), 7.18–7.21 (m, 2 H), 7.46–7.50 (m, 6 H), 7.54–7.59 (m, 3 H), 7.69–7.74 (m, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 113.8, 117.3, 118.9, 119.7 (d, J_{CP} = 9 Hz), 123.9, 124.6, 128.9 (d, J_{CP} = 12 Hz), 129.2, 130.3 (d, J_{CP} = 100 Hz), 132.2 (d, J_{CP} = 3 Hz), 132.6 (d, J_{CP} = 10 Hz), 136.1 (d, J_{CP} = 19 Hz), 140.9, 142.7. MS (EI) *m*/*z* (%) = 514 (76), 513 (50), 512 [M$^+$] (100), 501 (35), 386 (11), 262 (65), 215 (11). HRMS (EI): Calcd for $C_{30}H_{23}N_2P^{35}Cl_2$: 512.0976; found: 512.0977.

4.3.5 | 5-Chloro-1-*N*-(1,3-benzothiazol-2-yl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3j)

Orange crystals, mp: 210–213°C; yield: 360 mg, (67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.44–6.47 (m, 1 H), 6.58–6.63 (m, 1 H), 6.75–6.79 (m, 1 H), 7.10–7.14 (m, 1 H), 7.30–7.34 (m, 1 H), 7.46–7.50 (m, 6 H), 7.53–7.58 (m, 3 H), 7.61–7.64 (m, 1 H), 7.65–7.69 (m, 1 H), 7.72–7.77 (m, 6 H), 7.16–8.19 (m, 1 H), 9.33 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.9, 117.8, 119.3, 119.5, 120.5, 121.8, 121.9, 125.7, 128.8 (d, J_{CP} = 11 Hz), 130.3 (d, J_{CP} = 99 Hz), 130.5, 132.0, 132.5 (d, J_{CP} = 10 Hz), 134.3 (d, J_{CP} = 20 Hz), 139.1, 152.7, 162.5. MS (EI) *m*/*z* (%) = 501 [M$^+$] (100), 500 (27), 392 (12), 352 (10), 262 (56). HRMS (EI): Calcd for $C_{31}H_{24}N_3PS$: 501.1429; found: 501.1441.

4.3.6 | 1-*N*-(2,6-Dimethylphenyl)-5-(morpholin-1-yl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3k)

Fine green crystals, mp: 178–181°C; yield: 156 mg, (28%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.21 (s, 6 H), 2.84–2.87 (m, 4 H), 3.71–3.73 (m, 4 H), 5.79 (s, 1 H), 5.89–5.94 (m, 1 H), 6.37–6.41 (m, 1 H), 6.84–6.86 (m, 1 H), 7.02–7.12 (m, 3 H), 7.42–7.54 (m, 9 H), 7.74–7.81 (m, 6 H). ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 18.6, 50.8, 67.2, 100.1, 104.0, 119.3, 124.8, 128.2, 128.5 (d, J_{CP} = 11 Hz), 131.1, 131.6 (d, J_{CP} = 98 Hz), 131.6, 132.5 (d, J_{CP} = 9 Hz), 135.9, 140.5, 144.1, one signal invisible. MS (ESI) *m/z* (%) = 558.27 $[M+H]^+$. HRMS (EI): Calcd for $C_{36}H_{37}N_3PO$: 558.2674; found: 558.2676.

4.3.7 | 3-[(4-Cyanophenyl)amino]-4-[(triphenyl-λ^5-phosphanylidene)amino] benzonitrile (3l)

Fine white crystals, mp: 201–204°C; yield: 375 mg, (76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.36–6.40 (m, 1 H), 6.82–6.85 (m, 1 H), 7.14–7.18 (m, 2 H), 7.49–7.55 (m, 9 H), 7.59–7.63 (m, 3 H), 7.66–7.71 (m, 6 H), 7.92 (br s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 99.0, 102.0, 116.2, 117.2, 119.5 (d, J_{CP} = 10 Hz), 120.0, 120.9, 126.2, 129.1 (d, J_{CP} = 12 Hz), 129.2 (d, J_{CP} = 101 Hz), 132.5 (d, J_{CP} = 10 Hz), 132.7 (d, J_{CP} = 3 Hz), 133.9, 135.4 (d, J_{CP} = 21 Hz), 145.9, 147.0. MS (EI) *m/z* (%) = 494 $[M^+]$ (100), 493 (34), 263 (12), 262 (14), 183 (51). HRMS (EI): Calcd for $C_{32}H_{23}N_4P$: 494.1660; found: 494.1658.

4.3.8 | 5-Chloro-1-*N*-(2-naphtyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3m)

Fine green crystals, mp: 71–74°C; yield: 269 mg (51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.34–6.36 (m, 1 H), 6.40–6.43 (m, 1 H), 7.26–7.33 (m, 2 H), 7.36–7.38 (m, 1 H), 7.39–7.42 (m, 1 H), 7.44–7.48 (m, 6 H), 7.51–7.56 (m, 3 H), 7.59–7.62 (m, 1 H), 7.69–7.77 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.0, 112.6, 118.7, 120.1 (d, J_{CP} = 9 Hz), 121.3, 122.7, 123.4, 126.4, 126.7, 127.7, 128.9 (d, J_{CP} = 12 Hz), 129.1, 129.2, 130.7 (d, J_{CP} = 99 Hz), 132.1 (d, J_{CP} = 12 Hz), 132.6 (d, J_{CP} = 10 Hz), 134.9, 137.8, 138.9 (d, J_{CP} = 20 Hz), 140.9. MS (EI) *m/z* (%) = 530 (47), 529 (51), 528 $[M^+]$ (100), 262 (50), 261 (14), 183 (46). HRMS (EI): Calcd for $C_{34}H_{26}N_2{}^{35}ClP$: 528.1522; found: 528.1532.

4.3.9 | 1-*N*-(4-Chlorophenyl)-4-methyl-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3n)

Fine gray crystals; mp: 204–206°C; yield: 274 mg, (56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 3 H), 6.26–6.32 (m, 1 H), 6.43–6.46 (m, 1 H), 7.03–7.18 (m, 5 H), 7.27–7.31 (m, 1 H), 7.43–7.57 (m, 9 H), 7.67–7.77 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 114.7, 118.0, 118.1, 121.5 (d, J_{CP} = 9 Hz), 123.5, 128.8 (d, J_{CP} = 12 Hz), 129.0, 129.4, 130.9 (d, J_{CP} = 100 Hz), 131.9, 132.6 (d, J_{CP} = 10 Hz), 134.6 (d, J_{CP} = 20 Hz), 140.0, 143.7. MS (EI) *m/z* (%) = 494 (49), 492 (100), 366 (12), 262 (59), 183 (51), 108 (31). HRMS (EI): Calcd for $C_{31}H_{26}N_2{}^{35}ClP$: 492.1522; found: 492.1513.

4.3.10 | 1-*N*-(4-Chlorophenyl)-4-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3o)

Fine gray crystals; mp: 204–206°C; yield: 138 mg, (27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 6.10–6.12 (m, 1 H), 6.22–6.25 (m, 1 H), 6.95–7.01 (m, 3 H), 7.10–7.15 (m, 3 H), 7.40–7.46 (m, 6 H), 7.50–7.55 (m, 3 H), 7.67–7.72 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 102.1, 107.7 (d, J_{CP} = 10 Hz), 117.0, 117.2, 123.1, 128.8 (d, J_{CP} = 12 Hz), 129.0, 130.8 (d, J_{CP} = 100 Hz), 138.9 (d, J_{CP} = 19 Hz), 132.0 (d, J_{CP} = 2 Hz), 132.6 (d, J_{CP} = 9 Hz), 142.3, 144.6, 154.3. MS (EI) *m/z* (%) = 510 (48), 508 (100), 493 (36), 262 (51), 183 (44), 108 (30). HRMS (EI): Calcd for $C_{31}H_{26}N_2O^{35}ClP$: 508.1471; found: 508.1494.

4.3.11 | 1-*N*-Butyl-5-chloro-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3p)

Gray oil; yield: 124 mg, (27%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.3 Hz, 3 H), 1.43–1.50 (m, 2 H), 1.64–1.71 (m, 2 H), 3.12–3.16 (m, 2 H), 5.30 (br s, 1 H), 6.19–6.21 (m, 2 H), 6.44–6.46 (m, 1 H), 7.43–7.47 (m, 6 H), 7.51–7.55 (m, 3 H), 7.69–7.74 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.6, 31.8, 43.7, 108.4, 114.9, 118.9 (d, J_{CP} = 9 Hz), 123.4, 128.7 (d, J_{CP} = 12 Hz), 131.0 (d, J_{CP} = 99 Hz), 131.9 (d, J_{CP} = 2 Hz), 132.6 (d, J_{CP} = 9 Hz), 135.8, 145.0 (d, J_{CP} = 19 Hz). MS (EI) *m/z* (%) = 460 (48), 459 (44), 458 $[M^+]$ (100), 415 (57), 262 (51), 183 (64). HRMS (EI): Calcd for $C_{28}H_{28}N_2P^{35}Cl$: 458.1679; found: 458.1679.

4.3.12 | 1-*N*-tert-Butyl-5-chloro-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (3q)

Fine yellow crystals, mp: 149–152°C; yield: 363 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (s, 9 H), 5.62 (br s, 1 H), 6.20–6.23 (m, 2 H), 6.74–6.77 (m, 1 H), 7.41–7.45 (m, 6 H), 7.49–7.54 (m, 3 H), 7.67–7.73 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.1, 50.9, 112.5, 115.5, 119.2 (d, J_{CP} = 9 Hz), 122.7, 128.7 (d, J_{CP} = 12 Hz), 131.2 (d, J_{CP} = 99 Hz), 131.8 (d, J_{CP} = 3 Hz), 132.6 (d, J_{CP} = 10 Hz), 137.4, 143.4 (d, J_{CP} = 19 Hz). MS (EI) *m/z* (%) = 460 (18), 459 (44), 458 $[M^+]$ (87), 445 (48), 443 (100), 262 (36), 247 (16). HRMS (EI): Calcd for $C_{28}H_{28}N_2{}^{35}ClP$: 458.1679; found: 458.1658.

4.3.13 | 6-Chloro-1-(4-chlorophenyl)-1H-benzimidazole (4)

Fine white crystals, mp: 126–129°C; yield: 63 mg (24%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.97 (br s, 1 H), 6.68–6.70 (m, 1 H), 6.71–6.73 (m, 1 H), 6.94–6.96 (m, 1 H), 7.04–7.09

(m, 2 H), 7.25–7.30 (m, 2 H), 7.39–7.41 (m, 2 H), 7.65–7.68 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 110.5, 121.5, 123.9, 125.4, 130.0, 130.5, 134.2, 134.5, 142.2, 142.6, one signal invisible. MS (ESI) *m*/*z* (%) = 263.01 $[M+H]^+$. HRMS (EI): Calcd for $C_{13}H_9N_2{}^{35}Cl_2$: 263.0143; found: 263.0139.

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