Synthesis of 1-arylbenzimidazoles and dibenzo[*b*,*e*][1,4]diazepines from 2-(arylamino)aryliminophosphoranes

E. Łukasik and Z. Wróbel *

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland
E-mail: zbigniew.wrobel@icho.edu.pl

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Abstract
2-(Arylamino)aryliminophosphoranes, easily obtained from 2-nitrosodiarylamines,were found to be convenient starting materials for simple reactions with common acylating reagents such as acid chlorides and the Vilsmeier reagent. The reactions allow for the synthesis of 1,2-disubstituted benzimidazoles or dibenzo[*b*,*e*][1,4]diazepines, depending on the substituents on the 2-arylamine nitrogen atom.

Keywords: Annulation, benzimidazoles, cyclization, nitroso compounds, dibenzodiazepines

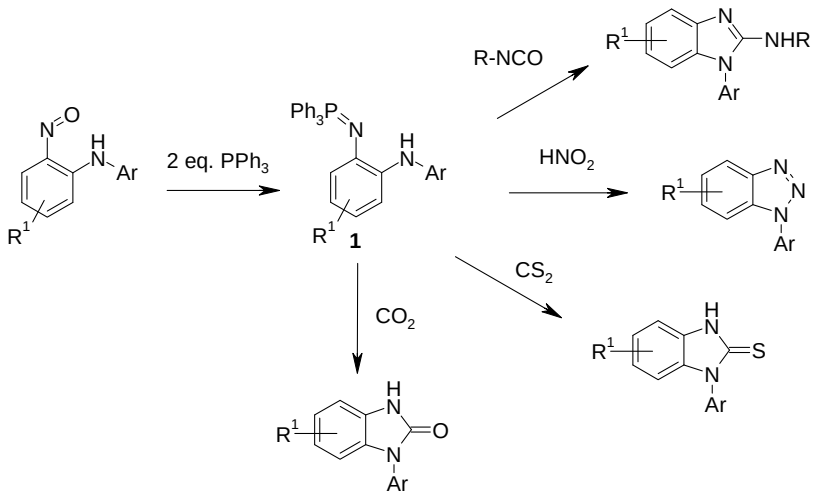
Introduction

In 2007 we described the synthesis of 2-nitrosodiarylamines from nitroarenes and anilines in the presence of the strong base *t*-BuOK.[1,2] The reaction, which proceeded via reductive substitution of aromatic hydrogen, did not require the presence of a nucleofuge group and allowed for the synthesis of a number of 2-arylamino-substituted nitrosoarenes. The latter, bearing two differently polarized groups, proved to be valuable starting materials in the synthesis of various nitrogen heterocycles.[3-8]

An attractive transformation of 2-nitrosodiarylamines appeared to be their smooth reaction with triphenylphosphine, first published in 2014,[9] leading to 2-(arylamino)arylimino-phosphoranes via a Cadogan-type reaction. These turned out to be versatile and stable equivalents for 1-aryl-1,2-arylenediamines; they reacted with isocyanates,[9] nitrous acid,[10] CS_2[11] and CO_2[12] furnishing 2-aminobenzimidazoles, benzotriazoles, 2-thiobenzimidazoles and 2-benzimidazolones respectively (Scheme 1).

While a nitroso group is unequivocally electrophilic in nature, it exhibits moderate nucleophilic character, originating in the lone electron pair on the nitrogen atom. Intramolecular nucleophilic reactions of nitroso nitrogen atoms are very rare, although the lone electron pair of

nitrogen is believed to be involved in certain cyclization processes.[13] Transformation of a nitroso group into an iminophosphorane group makes this nitrogen centre definitely nucleophilic due to charge separation in the ylide-like structure, which determines the reactivity of iminophosphoranes towards electrophiles, parallel to that of carbon-centred phosphorus ylides.[14]



Scheme 1. Synthesis and synthetic applications of 2-(arylamino)aryliminophosphoranes.

In 2-(arylamino)aryliminophosphoranes **1**, however, there is one more nucleophilic nitrogen atom, that of the arylamine substituent at the conjugated position 2. This arrangement creates a system in which both nitrogen atoms, and to some extent also the *N*-aryl ring, become disposed to reactions with electrophilic reagents. From our previous work it became clear that reactions of **1** with alkyl isocyanates, CS_2 and CO_2 proceed via initial addition of the iminophosphorane nitrogen atom to the carbonyl group of the other reagent, while the reactions with nitrous acid, leading to the benzotriazole system, seems to proceed in two different ways, including one involving initial nitrosation of the arylamine nitrogen atom.[10]

In this paper we present the results of reactions of 2-(arylamino)aryliminophosphoranes (**1**) with simple acylating agents such as acid chlorides and Vilsmeier reagents. Although both kinds of reagents are widely used for the introduction of a carbonyl function into nucleophilic centres, the Vilsmeier reaction is mainly known for the formylation of electron rich aromatic and hetero-aromatic rings.[15-17] The reactions of iminophosphoranes with acyl chlorides, esters or acid anhydrides are well known,[18-22] and are useful for the synthesis of various heterocyclic systems.[23-29] The initial step of the reaction is always the addition of the nitrogen atom of the iminophosphorane to the carbonyl double bond followed by elimination of triphenylphosphine oxide, resulting in an imine function, which is prone to further intramolecular cyclization. Thus, it proceeds according to the standard aza-Wittig reaction scheme,[14] and such a process could be expected to occur in the case of **1**. An alternative process, i.e. initial acylation of the nitrogen

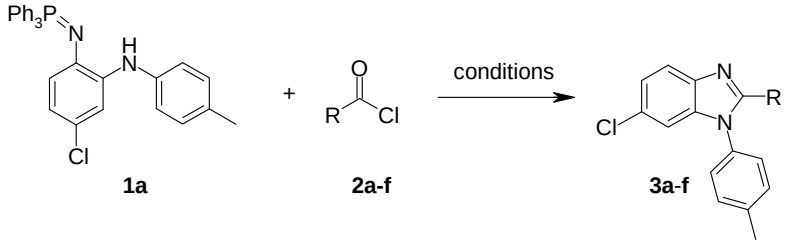
atom of the *ortho* arylamino group, would however lead, after the subsequent aza-Wittig cyclization, to the same products.

To our knowledge, there are no published reports dealing with the interaction of imino-phosphoranes with Vilsmeier reagents. The expected outcome of the reaction of the latter with **1** is a typical acylation of the aromatic para or ortho carbon atom in the arylamine moiety.[15-17] If this process could occur at the ortho position, it could then via subsequent intramolecular aza-Wittig reaction[14] lead to dibenzodiazepine derivatives. This was the most attractive option among the considered reaction routes.

Results and Discussion

In order to test the above predictions, different 2-(arylamino)aryliminophosphoranes **1** were reacted with both types of acylating agent. For the reaction with aliphatic and aromatic acid chlorides the model iminophosphorane **1a** was selected and Et_3N in MeCN at elevated temperature, the most common reaction conditions for acylation reactions,[23] were used. In the all successful reactions expected 2-aryl-1,2-benzimidazoles **3a**-**f**, as a result of the 5-membered ring cyclization, were isolated exclusively (Table 1). Only in one case of pivaloyl chloride, the standard MeCN/Et_3N system was not suitable, and more robust conditions were necessary to

Table 1. Results of the reaction of model iminophosphorane **1a** with various acyl chlorides (**2**)

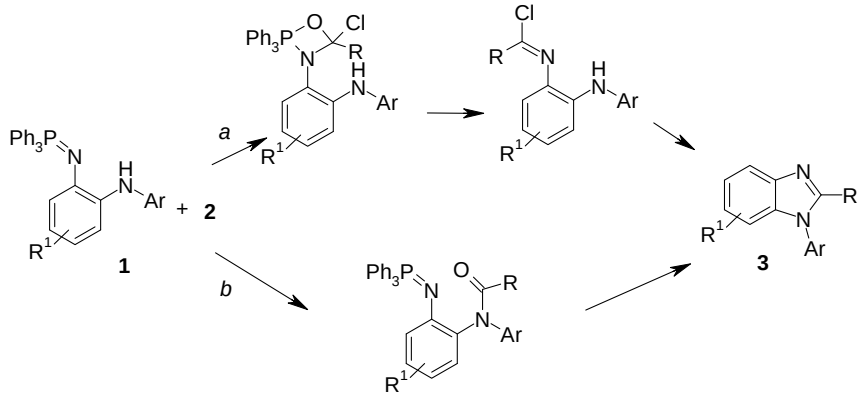


Entry	R	**2**	Reaction conditions	**3**	Yield[a] (%)
1	C_6H_5	**2a**	MeCN, NEt_3, 70 °C / 2 h	**3a**	94
2	4-ClC_6H_4	**2b**	MeCN, NEt_3, 70 °C / 2 h	**3b**	77
3	3-ClC_6H_4	**2c**	MeCN, NEt_3, 70 °C / 2 h	**3c**	46
4	CH_2=CH	**2d**	MeCN, NEt_3, 70 °C / 2 h	**3d**	56
5	$CH_3(CH_2)_4$	**2e**	MeCN, NEt_3, 70 °C / 2 h	**3e**	90
6	*t*-Bu	**2f**	MeCN, NEt_3, 70 °C / 24 h	-	-[b]
7	*t*-Bu	**2f**	Pyridine, 100 °C / 24 h	**3f**	78
8	Me_2N	**2g**	[c]	-	-[b]

[a]Isolated yield; [b]A multicomponent mixture; [c] Various conditions: *n*-BuLi, THF, r.t. 5 h; *t*-BuOK, THF, r.t. 5 h; MeCN, NEt_3, 70 °C, 24 h

obtain satisfactory yields of the products (Table 1, entries 6 and 7). For the poorly electrophilic dimethylcarbamoyl chloride the reaction was tried under various conditions but without success.

The results did not provide any indications regarding the most plausible sequence of the reaction steps (Scheme 2). It can proceed according to the standard aza-Wittig reaction scheme (path a), and such a process could be expected in the case of **1**, but, as pointed out in the Introduction, the alternative of acylation of the amine nitrogen of the *ortho*-arylamino group (path *b*) would lead, after a subsequent aza-Wittig cyclization, to the same products.



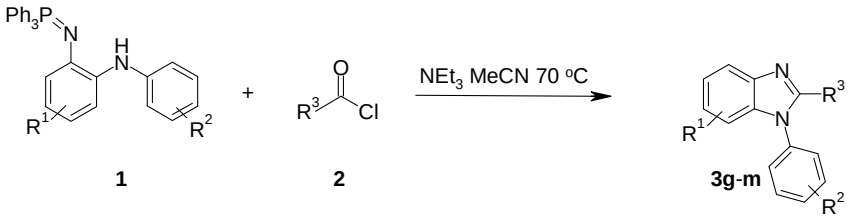
Scheme 2. Possible routes for the formation of **3**.

The results with the above simple procedure encouraged us to expand the method for other iminophosphoranes **1**, and thus, to synthesize the various differently substituted benzimidazoles **3g-m** (Table 2).

The reaction appeared to be a quite general, easy and useful method for the synthesis of 1,2-disubstituted benzimidazoles, as a final step of the synthetic route from simple nitroarenes through *N*-aryl-2-nitrosoanilines[1,2] and the corresponding iminophosphoranes. The yields are high and independent of the substituents present in both aromatic rings, and of the acid chloride used. Thus, both aromatic and aliphatic substituents could be introduced in position 2 of the resulting benzimidazoles. It should be pointed out that the entire method, starting from simple nitroarenes through 2-nitrosoanilines and iminophosphoranes, widens the choice of regio-selective methods available for the synthesis of 1,2-disubstituted benzimidazoles.[30]

The reactions of **1** with the Vilsmeier reagent gave somewhat different results and shed some light on the mechanism of the acylation process. The Vilsmeier reagent was prepared from DMF and $POCl_3$, and then the reaction with iminophosphoranes **1** was carried out in dichloroethane (DCE) at room temperature over several hours, followed by a usual aqueous work-up. In none of the cases, however, was formation of a seven-membered fused system observed. Instead, 1-arylbenzimidazoles were obtained, mostly in high yields (Table 3).

Table 2. Synthesis of 2-substituted 1-arylbenzimidazoles **3** from iminophosphoranes **1**

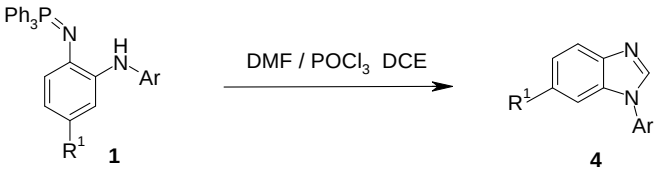


Entry	Iminophosphorane			Acyl chloride		Reaction time (h)	3	Yield[a] (%)
	R^1	R^2	**1**	R^3	**2**			
1	H	H	**1b**	Ph	**2a**	1	**3g**	98
2	4-OMe	4-Br	**1c**	Ph	**2a**	1	**3h**	97
3			**1c**	$CH_3(CH_2)_4$	**2e**	2	**3i**	89
4	4-Cl	2-I-4-Me	**1d**	Ph	**2a**	4	**3j**	94
5	4-OMe	4-Me	**1e**	Ph	**2a**	1.5	**3k**	89
6			**1e**	4-ClC_6H_4	**2b**	1	**3l**	88
7	H	H	**1b**	4-ClC_6H_4	**2b**	1	**3m**	97

[a] Isolated yield.

Such reaction products suggest the reaction course analogous to that considered previously for the acylation of **1** with acid chlorides (Scheme 3).

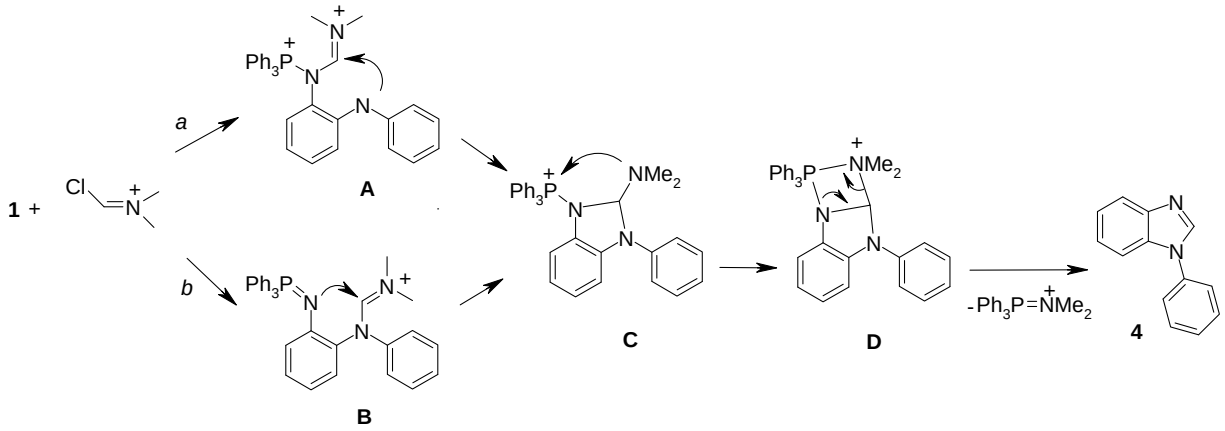
Table 3. Synthesis of *N*-arylbenzimidazoles **4** in the reaction of **1** with the Vilsmeier reagent



Entry	**1**	R^1	Ar	**4**	Yield[a] (%)
1	**1a**	Cl	4-MeC_6H_4	**4a**	97
2	**1f**	Br	4-MeC_6H_4	**4b**	86
3	**1g**	F	4-ClC_6H_4	**4c**	73
4	**1e**	OMe	4-MeC_6H_4	**4d**	88
5	**1h**	2-OMe-4-Cl	4-$EtOC_6H_4$	**4e**	76
6	**1i**	F	4-MeC_6H_4	**4f**	20

[a] Isolated yield

Both path *a* and *b* involve formation of structure **C**, followed by creation of a four-membered ring in structure **D**, similarly to the known aza-Wittig condensation. In this case, however, a double-aza variant would takes place, unprecedented in the known literature. On the other hand, classical aza-Wittig condensation involving a carbonyl group had to be preceded by hydrolysis of the imino function, which seems unlikely as the reaction conditions are rather anhydrous.



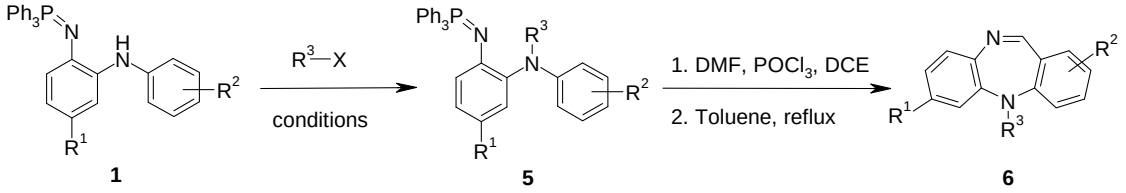
Scheme 3. The Vilsmeier route to 1-arylbenzimidazoles.

Clarification of the reaction course required additional experiments. Firstly, the arylamine nitrogen atom was blocked by an alkyl group in order to be protected against any irreversible addition. Thus, *N*-alkylated iminophosphoranes **5** were obtained by deprotonation of **1** with NaH/DMF or n-BuLi/THF, followed by the alkylation with appropriate alkyl halide. The products, furnished in moderate to good yields (Table 4), reacted with Vilsmeier reagent as presented in the experimental. The desired dibenzodiazepines **6** were isolated in mediocre to good yields (Table 4).

The alkylation of the amine nitrogen atom prevented both its initial addition to the Vilsmeier reagent (path *b* in Scheme 3) and cyclization leading to intermediate **C** (path *a* in Scheme 3). Consequently, formation of the seven-membered ring became possible. It was not clear, however, whether it was a result of the initial *ortho* formylation of the aryl ring, or of the cyclization of the alkylated intermediate, analogous to **A** (in Scheme 3), engaging the activated *ortho* position in the aromatic ring. In an additional experiment, the reaction of **5d** was repeated, but the crude polar intermediate was isolated and analyzed. Although complete identification of the intermediate from the NMR spectra was not achieved, it was found that the main product contained a triphenylphosphine moiety, a dimethylamino group and the side *N*-aryl ring lacking any new substituent. This last fact enabled us to eliminate from mechanistic consideration the *ortho*-formylation of the aromatic ring. Therefore it seems reasonable to consider initial addition of the strongly nucleophilic iminophosphorane nitrogen to the chloroiminium reagent as the first step of the reaction. The diarylamine nitrogen atom is available for the formation of a five-

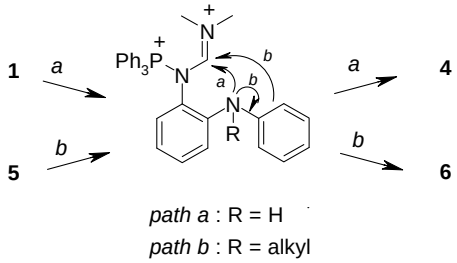
membered ring only if it is not further substituted. Otherwise, reaction with the Vilsmeier reagent leads to seven-membered ring formation (Scheme 4).

Table 4. Synthesis of 5-alkylated dibenzo[*b*,*e*][1,4]diazepines **6** from 2-(arylamino)aryliminophosphoranes **1**



Entry	R^1	R^2	**1**	R^3	Conditions[a] (time, h)	**5**	Yield[b] (%)	**6**	Yield[b] (%)
1	F	4-Me	**1i**	C_4H_9	B (24)	**5a**	53	**6a**	69
2	F	4-Me	**1i**	CH_2=$CHCH_2$	B (4)	**5b**	88	**6b**	10
3	Cl	4-MeO	**1j**	C_4H_9	A (20)	**5c**	64	**6c**	12
4	Cl	4-Me	**1a**	C_4H_9	B (24)	**5d**	86	**6d**	48
5	Cl	4-Me	**1a**	CH_2=$CHCH_2$	B (24)	**5e**	79	**6e**	25
6	Br	4-Me	**1f**	C_4H_9	A (20)	**5f**	80	**6f**	69
7	Br	4-Me	**1f**	CH_2=$CHCH_2$	B (24)	**5g**	67	**6g**	33
8	Br	4-Me	**1f**	Bn	A (20)	**5h**	80	**6h**	36
9	Ph	4-Me	**1k**	C_4H_9	C (24)	**5i**	39	**6i**	40

[a] A: NaH/DMF; B: BuLi/THF; C: BuLi/THF/HMPA [b] Isolated yield



Scheme 4. Different reactions paths depending on the arylamine nitrogen substitution.

The majority of known methods for the formation of the dibenzo[1,4]diazepine central ring require reactive functions to be present at the ortho positions of both diarylamine rings of the intermediate.[31] Only a few processes corresponding to the present reaction course could be found in the literature, primarily related to the high temperature cyclization of ortho-placed amide function with N unsubstituted ortho position in the other aryl ring, carried out in $POCl_3$ and

PPA.[32-35] Interestingly, also in those reactions seven-membered rings are formed only in cases where the diarylamine nitrogen atom is alkylated.[31,35]

In contrast to the Vilsmeier reagent, acyl chlorides did not react with *N*-alkylated iminophosphoranes **5** under the conditions used for successful cyclocondensation of **1**, and no products were formed after prolonged reaction times at elevated temperature. Apparently, acylation of **1** with acyl chlorides occurs at the amine nitrogen atom according to path *b* in Scheme 2, the route which is precluded in the case of **5**.

Conclusions

2-(Arylaminoaryl)iminophosphoranes, easily obtained from 2-nitrosodiarylamines, have proved to be convenient starting materials leading to important fused nitrogen heterocyclic systems for simple reactions with common acylating agents such as acyl chlorides and Vilsmeier reagent, High yielding cyclocondensation with acyl chlorides provided 1,2-disubstituted benzimidazoles while the reaction with Vilsmeier reagent allowed for the synthesis of *N*-arylbenzimidazoles or dibenzo[*b*,*e*][1,4]diazepines, depending on the substituents on the 2-arylamine nitrogen atom.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 400 MHz and 500 MHz instruments at 298 K. Chemical shifts are expressed in ppm referred to TMS (^{1}H NMR at 400 and 500 MHz) or to the solvent used (^{13}C NMR at 100 and 125 MHz respectively), with coupling constants in Hertz. Mass spectra were obtained on a AutoSpec Premier (Waters) spectrometer (EI, 70 eV). Silica gel Merck 60 (230-400 mesh) was used for column chromatography. THF was distilled from sodium/benzophenone ketyl prior to use. DMF was dried over CaH_2, distilled and stored over molecular sieves.

Common reagents and materials were purchased from commercial sources and used as received.

Preparation and characterization of 2-(arylamino)aryliminophosphoranes **1** have been described in our previous papers.[9-12]

General procedure for the reactions of iminophosphoranes **1** with acyl chlorides: To a solution of iminophosphorane **1** (1 mmol) and benzoyl chloride **2** (1.1 mmol) in CH_3CN (10 mL) was added NEt_3 (2 mmol). The mixture was stirred at reflux temperature for the time specified in Table 1. When the reaction was complete it was cooled to room temperature. After evaporation, the crude product was purified on column chromatography (SiO_2, hexane/ethyl acetate, 9:1 to 2:1). Solid products were recrystallised from hexane/ ethyl acetate mixture.

6-Chloro-1-(4-methylphenyl)-2-phenyl-1*H*-benzimidazole (3a). Colourless fine crystals, yield 300 mg (94%), mp 165-167 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 7.08-7.11 (m, 2H),

7.15 (d, *J* 1.9 Hz, 1H), 7.18-7.20 (m, 1H), 7.21-7.25 (m, 4H), 7.26-7.30 (m, 1H), 7.48-7.51 (m, 2H), 7.69 (d, *J* 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 110.6, 120.6, 123.5, 127.0, 128.3, 128.9, 129.3, 129.6, 130.6, 133.9, 138.0, 139.0, 141.6, 153.2, [one signal invisible]. MS (EI): *m/z* (%) 320 (35), 319 (47), 318 (100), 317 (81), 282 (15). HRMS (EI): *m/z* calcd for $C_{20}H_{15}N_2{}^{35}Cl$: 318.0924, found: 318.0916.

6-Chloro-2-(4-chlorophenyl)-1-(4-methylphenyl)-1*H*-benzimidazole (3b). Colourless fine crystals, yield 272 mg (77%), mp 165-168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.46 (s, 3H), 7.15-7.20 (m, 3H), 7.27-7.34 (m, 5H), 7.50-7.52 (m, 2H), 7.76 (d, *J* 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 110.6, 120.6, 123.8, 127.0, 128.0, 128.7, 129.2, 130.5, 130.8, 133.6, 135.9, 137.9, 139.3, 141.3, 152.0. MS (EI): *m/z* (%) 356 (11), 355 (21), 354 (20), 353 (66), 352 (66), 351 (100), 350 (70). HRMS (EI): *m/z* calcd for $C_{20}H_{14}{}^{35}Cl_2N_2$: 352.0534; found: 352.0533.

6-Chloro-2-(3-chlorophenyl)-1-(4-methylphenyl)-1*H*-benzimidazole (3c). Colourless fine crystals, yield 162 mg (46%), mp 134-136 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (s, 3H), 7.16-7.22 (m, 4H), 7.29-7.35 (m, 5H), 7.70 (s, 1H), 7.77 (d, *J* 8.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 110.7, 120.8, 123.8, 126.9, 127.2, 129.3, 129.4, 129.5, 129.7, 130.8, 131.3, 133.5, 134,5, 138.0, 139.4, 141.4, 151.6. MS (EI): *m/z* (%) 356 (11), 355 (20), 354 (66), 353 (62), 352 (100), 351 (64). HRMS (EI): *m/z* calcd for $C_{20}H_{14}{}^{35}Cl_2N_2$: 352.0534, found: 352.0525.

6-Chloro-1-(4-methylphenyl)-2-vinyl-1*H*-benzimidazole (3d). Brown oil, yield 150 mg (56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.47 (m, 3H), 5.57-5.60 (dd, *J* 8.6, 3.9 Hz, 1H), 6.49-6.52 (m, 2H), 7.13 (d, *J* 2.0 Hz, 1H), 7.22-7.25 (m, 3H), 7.36-7.39 (m, 2H), 7.69 (d, *J* 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 110.3, 120.4, 123.2, 123.5, 123.6, 127.1, 128.8, 130.5, 132.3, 137.1, 139.4, 141.4, 151.2. MS (EI): *m/z* (%) 270 (36), 269 (35), 268 (100), 267 (51), 255 (19), 254 (13), 253 (59), 233 (15), 218 (16). HRMS (EI): *m/z* calcd for $C_{16}H_{13}{}^{35}ClN_2$: 268.0767, found: 268.0773.

2-Pentyl-6-chloro-1-(4-methylphenyl)-1*H*-benzimidazole (3e). Colourless fine crystals, yield 280 mg (90%), mp 61-63 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81-0.84 (m, 3H), 1.25-1.29 (m, 4H), 1.75-1.80 (m, 2H), 2.48 (s, 3H), 2.70-2.75 (m, 2H), 7.05 (s, 1H), 7.18-7.23 (m, 3H), 7.35-7.39 (m, 2H), 7.64-7.67 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 21.2, 22.2, 27.4, 27.6, 31.4, 110.1, 119.8, 122.7, 127.0, 128.1, 130.6, 132.8, 137.2, 139.3, 141.2, 156.4. MS (EI): *m/z* (%) 314 (13), 313 (11), 312 (36), 283 (12), 271 (28), 270 (27), 269 (74), 258 (37), 257 (43), 256 (100). HRMS (EI): *m/z* calcd for $C_{19}H_{21}{}^{35}Cl_2N_2$: 312.1393; found: 312.1388.

2-*tert*-Butyl-6-chloro-1-(4-methylphenyl)-1*H*-benzimidazole (3f). Colourless fine crystals, yield 232 mg (78%), mp 179-181 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (m, 9H), 2.41 (m, 3H), 6.66 (d, *J* 1.5 Hz, 1H), 7.10-7.16 (m, 3H), 7.26-7.29 (m, 2H), 7.60 (d, *J* 8.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 30.1, 35.1, 110.1, 119.9, 122.6, 128.2, 129.0, 130.2, 134.8, 139.7, 139.8, 162.5 (one signal not found). MS (EI): *m/z* (%) 300 (23), 299 (20), 298 (69), 285 (35), 283 (100), 267 (14), 241 (15), 195 (30), 193 (89), 166 (16). HRMS (EI): *m/z* calcd for $C_{18}H_{19}{}^{35}Cl_2N_2$: 298.1237; found: 298.1235.

1,2-Diphenyl-1*H*-benzimidazole (3g). Colourless fine crystals, yield 265 mg (98%), mp 93-96 °C (lit.[36] mp: 86-87 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.35 (m, 8H), 7.47-7.60 (m, 5H),

7.85-7.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.6, 120.0, 123.1, 123.5, 127.6, 128.4, 128.7, 129.5, 129.6, 130.0, 130.1, 137.2, 137.4, 143.2, 152.5.

1-(4-Bromophenyl)-6-methoxy-2-phenyl-1*H*-benzimidazole (3h). Colourless fine crystals, yield 367 mg (97%), mp 153-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.66 (d, *J* 4.0 Hz, 1H), 6.95-6.99 (dd, *J* 8.0, 4.0 Hz, 1H), 7.16-7.20 (m, 2H), 7.28-7.39 (m, 3H), 7.49-7.53 (m, 2H), 7.62-7.65 (m, 2H), 7.75 (d, *J* 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.0, 93.9, 112.5, 120.7, 122.5, 128.5, 129.1, 129.3, 129.5, 130.0, 133.3, 136.3, 137.7, 151.6, 157.4 (one signal not found). MS (EI): *m/z* (%) 380 (99), 378 (100), 365 (52), 255 (12), 153 (37). HRMS (EI): *m/z* calcd for $C_{20}H_{15}{}^{79}BrN_2O$: 378.0368; found: 378.0366.

1-(4-Bromophenyl)-6-methoxy-2-pentyl-1*H*-benzimidazole (3i). Colourless fine crystals, yield 332 mg (89%), mp 89-92 °C. ^{1}H NMR (400 M Hz, $CDCl_3$): δ 0.84-0.87 (m, 3H), 1.26-1.30 (m, 4H), 1.74-1.85 (m, 2H), 2.67-2.73 (m, 2H), 3.76 (s, 3H), 6.51-6.54 (m, 1H), 6.87-6.92 (m, 1H), 7.22-7.30 (m, 1H), 7.45-7.53 (m, 1H), 7.63-7.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.4, 27.6, 27.9, 31.6, 56.0, 93.8, 111.5, 119.9, 122.9, 129.1, 133.4, 135.4, 137.0, 137.2, 154.4, 156.9. MS (EI): *m/z* (%) 374 (31), 372 (32), 331 (70), 318 (96), 316 (100), 236 (25), 161 (40). HRMS (EI): *m/z* calcd for $C_{19}H_{21}{}^{79}BrN_2O$: 372.0837; found: 372.0841.

6-Chloro-1-(2-iodo-4-methylphenyl)-2-phenyl-1*H*-benzimidazole (3j). Colourless fine crystals, yield 420 mg (94%), mp 141-144 °C. ^{1}H NMR (400 M Hz, $CDCl_3$): δ 2.43 (s, 3H), 6.95-6.99 (m, 1H), 7.21-7.39 (m, 6H), 7.56-7.62 (m, 2H), 7.76-7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 98.4, 111.1, 120.9, 123.9, 128.6, 129.1, 129.2, 129.4, 129.9, 130.8, 137.0, 137.6, 141.1, 141.7, 141.8, 154.0. MS (EI): *m/z* (%) 446 (37), 444 (100), 319 (31), 317 (66), 316 (38), 282 (27). HRMS (EI): *m/z* calcd for $C_{20}H_{14}{}^{35}ClIN_2$: 443.9890; found: 443.9880.

6-Methoxy-1-(4-methylphenyl)-2-phenyl-1*H*-benzimidazole (3k). Colourless fine crystals, yield 280 mg (89%), mp 161-164 °C (lit.[3] 166-167 °C). The NMR and MS spectra in accord with literature data.[3]

2-(4-Chlorophenyl)-6-methoxy-1-(4-methylphenyl)-1*H*-benzimidazole (3l). Colourless fine crystals, yield 308 mg (88%), mp 166-169 °C. ^{1}H NMR (400 M Hz, $CDCl_3$): δ 2.46 (s, 3H), 3.78 (s, 3H), 6.65 (d, *J* 4.0 Hz, 1H), 6.94-6.97 (dd, *J* 8.0, 4.0 Hz, 1H), 7.15-7.19 (m, 2H), 7.24-7.27 (m, 2H), 7.29-7.33 (m, 2H), 7.45-7.49 (m, 2H), 7.73 (d, *J* 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 56.0, 112.6, 120.5, 127.2, 128.6, 128.9, 130.5, 130.8, 134.4, 135.3, 137.5, 138.2, 139.0, 150.6, 157.4, [one signal invisible]. MS (EI): *m/z* (%) 350 (38), 349 (30), 348 (100), 335 (22), 333 (11), 91 (13). HRMS (EI): *m/z* calcd for $C_{21}H_{17}{}^{35}ClN_2O$: 348.1029; found: 348.1029.

2-(4-Chlorophenyl)-1-phenyl-1*H*-benzimidazole (3m).[37] Colourless fine crystals, yield 294 mg (97%), mp 137-139 °C (lit.[38] 140-141 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-7.37 (m, 7H), 7.46-7.58 (m, 5H), 7.85-7.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.6, 120.0, 123.3, 123.7, 127.5, 128.6, 128.7, 128.9, 130.1, 130.8, 135.8, 136.9, 137.4, 143.1, 151.3.

General procedure for the synthesis of *N*-arylbenzimidazoles (4) in the reaction of (1) with the Vilsmeier reagent. $POCl_3$ (0.37 mL, 4 mmol) was added dropwise to DMF (0.31 mL, 4 mmol) at ~0 ºC, and the mixture were stirred for 10 min without cooling. A solution of **1** (1

mmol) in dichloroethane (5 mL) was then added dropwise at 25 ºC. The resulting mixture was stirred for 1 h at rt, then diluted aqueous K_2CO_3 (2 mL) was added and stirring was continued for 15 min. The mixture was extracted with ethyl acetate (3 × 20 mL), the combined organic phases were dried with Na_2SO_4 and the solvent was evaporated. The residue was purified on silica gel column chromatography (hexane/ethyl acetate, 9:1 to 2:1). Solid products were recrystallised from hexane/ ethyl acetate mixture.

6-Chloro-1-(4-methylphenyl)-1*H*-benzimidazole (4a). Colourless fine crystals, yield 234 mg (97%), mp 84-86 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.42 (s, 3H), 7.32-7.34 (dd, *J* 8.7 Hz, *J* 1.8 Hz, 1H), 7.42-7.45 (m, 2H), 7.55-7.58 (m, 3H), 7.78 (d, *J* 8.7 Hz, 1H), 8.57 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.6, 110.5, 121.2, 122.7, 123.7, 127.9, 130.5, 132.9, 133.9, 137.6, 142.5, 144.4. MS (EI): *m/z* (%) 244 (48), 243 (30), 242 (100), 241 (19). HRMS (EI): *m/z* calcd for $C_{14}H_{11}{}^{35}ClN_2$: 242.0611; found: 242.0607.

6-Bromo-1-(4-methylphenyl)-1*H*-benzimidazole (4b). Colourless fine crystals, yield 248 mg (86%), mp 102-105 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.42 (s, 3H), 7.42-7.46 (m, 3H), 7.54-7.58 (m, 2H), 7.69-7.75 (m, 2H), 8.55 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.6, 113.3, 115.8, 121.6, 123.8, 125.3, 130.5, 132.9, 134.4, 137.7, 142.8, 144.3. MS (EI): *m/z* (%) 288 (98), 287 (49), 286 (100), 285 (28), 207 (19), 192 (14), 180 (16). HRMS (EI): *m/z* calcd for $C_{14}H_{11}{}^{79}BrN_2$: 286.0106; found: 286.0119.

1-(4-Chlorophenyl)-6-fluoro-1*H*-benzimidazole (4c). Colourless fine crystals, yield 180 mg (73%), mp 240-243 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.35-7.39 (m, 1H), 7.63-7.66 (dd, *J* 9 Hz, *J* 2 Hz, 1H), 7.76-7.80 (m, 2H), 7.89-7.91 (m, 2H), 7.93-7.96 (m, 1H), 9.21 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 99.3 (d, J_{CF} 29 Hz), 113.3 (d, J_{CF} 26 Hz), 120.2 (d, J_{CF} 10 Hz), 127.1, 130.9, 133.7 (d, J_{CF} 14 Hz), 134.5, 134.7, 136.6, 144.2, 161.2 (d, J_{CF} 239 Hz). MS (EI): *m/z* (%) 248 (34), 246 (100), 211 (12), 184 (11). HRMS (EI): *m/z* calcd for $C_{13}H_8{}^{35}ClFN_2$: 246.0360; found: 246.0367.

6-Methoxy-1-(4-methylphenyl)-1*H*-benzimidazole (4d). Colourless oil. yield 210 mg (88%), ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.41 (s, 3H), 3.78 (s, 3H), 6.90-6.93 (dd, *J* 8.8 Hz, *J* 2.4 Hz, 1H), 7.01 (d, *J* 2.4 Hz, 1H), 7.41-7.44 (m, 2H), 7.53-7.57 (m, 2H), 7.64 (d, *J* 8.8 Hz, 1H), 8.35 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 21.1, 56.0, 94.1, 112.3, 120.8, 124.0, 130.9, 134.0, 134.3, 137.7, 138.5, 142.8, 157.1. MS (EI): *m/z* (%) 238 (100), 224 (12), 223 (66). HRMS (EI): *m/z* calcd for $C_{15}H_{14}N_2O$: 238.1106; found: 238.1115.

6-Chloro-1-(4-ethoxyphenyl)-4-methoxy-1*H*-benzimidazole (4e). Colourless fine crystals, yield 230 mg (76%), mp 75-78 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.37 (t, *J* 6.9 Hz, 3H), 3.99 (s, 3H), 4.11 (q, *J* 7.1 Hz, 2H), 6.85-6.87 (m, 1H), 7.07-7.08 (m, 1H), 7.13-7.16 (m, 2H), 7.53-7.55 (m, 2H), 8.38 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 15.0, 56.7, 63.9, 103.5, 105.4, 116.0, 126.1, 128.6, 128.9, 132.9, 135.8, 143.2, 152.2, 158.7. MS (EI): *m/z* (%) 304 (37), 303 (56), 302 (81), 301 (100), 275 (27), 274 (29), 273 (57), 272 (40). HRMS (EI): *m/z* calcd for $C_{16}H_{15}{}^{35}ClN_2O_2$: 302.0822; found: 302.0807.

6-Fluoro-1-(4-methylphenyl)-1*H*-benzimidazole (4f). Colourless oil. yield 46 mg (20%), ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.14 (s, 3H), 7.14 -7.19(m, 1H), 7.37-7.40 (dd, *J* 9.3 Hz, *J* 2.6

Hz, 1H), 7.42-7.45 (m, 2H), 7.55-7.58 (m, 2H), 7.77-7.80 (m, 1H), 8.54 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 21.0, 97.86 (d, J_{CF} 28 Hz), 111.0 (d, J_{CF} 25 Hz), 121.4 (d, J_{CF} 10 Hz), 124.0, 130.9, 133.6, 133.8 (d, J_{CF} 13 Hz), 138.0, 140.8, 144.7 (d, J_{CF} 3 Hz), 159.8 (d, J_{CF} 237 Hz). MS (EI): *m/z* (%) 226 (100), 225 (42). HRMS (EI): *m/z* calcd for $C_{14}H_{11}FN_2$: 226.0906; found: 226.0914.

General procedures for alkylation of iminophosphoranes (1)

Procedure A. NaH (60 percent in mineral oil, 10 mmol) was added under nitrogen to a solution of **1** (5 mmol) in DMF (15 mL). The mixture was stirred for 1 h, then the appropriate alkyl halide (15 mmol) was added and the resulting mixture was stirred at room temperature for the time specified in Table 4. The reaction mixture was poured into conc. aqueous NH_4Cl and extracted with EtOAc. The extract was dried with Na_2SO_4, then the solvent was evaporated. The crude product was subjected to column chromatography (SiO_2, hexane/ethyl acetate, 9:1 to 2:1).

Procedure B. To a cooled solution of **1** (5 mmol) in THF (20 mL) was added dropwise at –70 °C, under argon, *n*-BuLi (2.5 M in hexane, 2.2 mL, 5.5 mmol). The mixture was stirred at this temperature for 15 min then appropriate alkyl halide (15 mmol) was added dropwise. After that, the cooling bath was removed and the reaction mixture was stirred at rt. for the time specified (Table 4). The reaction mixture was then poured into water and extracted with EtOAc. The combined organic phases were dried Na_2SO_4. After evaporation, the crude product was subjected to column chromatography (hexane/ethyl acetate, 9:1 to 2:1). Solid products were recrystallised from hexane/ethyl acetate mixture.

1-*N*-Butyl-5-fluoro-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5a). Yellow oil, yield 1410 mg (53%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.77 (t, *J* 7.3 Hz, 3H), 1.24-1.29 (m, 2H), 1.47-1.54 (m, 2H), 2.14 (s, 3H), 3.64 (t, *J* 7.4 Hz, 2H), 6.30-6.34 (m, 1H), 6.48-6.51 (m, 2H), 6.56-6.62 (m, 1H), 6.84-6.88 (dt, J_{CF} 9.9 Hz, *J* 2.7 Hz, 1H), 6.89-6.92 (m, 2H), 7.43-7.48 (m, 6H), 7.51-7.58 (m, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.4, 20.3, 20.5, 30.2, 51.3, 112.5 (d, J_{CF} 21 Hz), 113.4, 116.5 (d, J_{CF} 22 Hz), 122.0 (d, J_{CP} 10 Hz), 124.4, 129.1 (d, J_{CF} 11 Hz), 130.5, 131.3, 132.2 (d, J_{CP} 2 Hz), 132.5 (d, J_{CP} 10 Hz), 140.4 (d, J_{CF} 9 Hz), 144.8 (d, J_{CP} 2 Hz), 146.8, 154.9 (d, J_{CF} 233 Hz). MS (EI): *m/z* (%) 532 (89), 490 (41), 489 (100), 426 (18), 370 (38), 263 (28), 262 (41), 241 (50), 227 (81). HRMS (EI): *m/z* calcd for $C_{35}H_{34}FN_2P$: 532.2444; found: 532.2465.

1-*N*-Allyl-5-fluoro-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5b). Colourless fine crystals, yield 2270 mg (88%), mp 129-132 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.20 (s, 3H), 4.33 (s, 2H), 5.00-5.10 (m, 1H), 5.27-5.40 (m, 1H), 5.88-6.00 (m, 1H), 6.41-6.60 (m, 4H), 6.82-6.94 (m, 3H), 7.23-7.60 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 54.4, 111.8 (d, J_{CF} 21 Hz), 114.3, 115.4, 115.7 (d, J_{CF} 21 Hz), 122.5 (d, J_{CF} 12 Hz), 125.4, 128.3 (d, J_{CP} 12 Hz), 128.9, 131.3 (d, J_{CP} 100 Hz), 131.4, 132.5 (d, J_{CP} 9 Hz), 135.7, 143.6, 146.3, 155.4, 156.5. MS (EI): *m/z* (%) 516 (100), 412 (13), 411 (47), 370 (45), 278 (31), 262 (86), 239 (82), 227 (45), 183 (77). HRMS (EI): *m/z* calcd for $C_{34}H_{30}FN_2P$: 516.2131; found: 516.2125.

1-*N*-Butyl-5-chloro-1-*N*-(4-methoxyphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5c). Yellow oil, yield 1805 mg (64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (t, *J* 7.3 Hz, 3H), 1.27-1.33 (m, 2H), 1.58-1.64 (m, 2H), 3.64 (t, *J* 7.5 Hz, 2H), 3.71 (s, 3H), 6.42-6.45 (m, 1H), 6.55-6.58 (m, 2H), 6.67-6.70 (m, 2H), 6.71-6.74 (dd, *J* 8.4 Hz, *J* 2.6 Hz, 1H), 7.10 (t, *J* 2.6 Hz, 1H), 7.35-7.39 (m, 6H), 7.46-7.54 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.0, 20.4, 30.1, 51.8, 55.9, 114.3, 114.7, 121.4, 123.2 (d, J_{CP} 10 Hz), 125.2, 128.3 (d, J_{CP} 12 Hz), 129.4, 130.6, 131.4 (d, J_{CP} 10 Hz), 132.5 (d, J_{CP} 10 Hz), 141.9 (d, J_{CP} 21 Hz), 143.5, 146.7, 151.0. MS (EI): *m/z* (%) 566 (41), 565 (41), 564 (100), 524 (12), 523 (36), 522 (34), 521 (94), 508 (24), 444 (11), 401 (27), 386 (40), 273 (38), 259 (90). HRMS (EI): *m/z* calcd for $C_{35}H_{34}{}^{35}ClN_2OP$: 564.2097; found: 564.2115.

1-*N*-Butyl-5-chloro-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5d). Yellow oil, yield 2357 mg (86%), ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.76-0.78 (m, 3H), 1.25-1.28 (m, 2H), 1.50-1.52 (m, 2H), 2.14 (s, 3H), 3.61-3.64 (m, 2H), 6.32-6.36 (m, 1H), 6.46-6.52 (m, 2H), 6.72-6.78 (m, 1H), 6.88-6.95 (m, 2H), 7.10-7.14 (m, 1H), 7.40-7.50 (m, 6H), 7.51-7.59 (m, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 13.9, 19.8, 20.0, 29.7, 50.9, 112.9, 119.7, 122.6 (d, J_{CP} 11 Hz), 123.9, 125.5, 128.7 (d, J_{CP} 12 Hz), 128.8, 129.3, 130.0 (d, J_{CP} 99 Hz), 131.8 (d, J_{CP} 2 Hz), 132.0 (d, J_{CP} 10 Hz), 140.7 (d, J_{CP} 22 Hz), 146.3, 147.1. MS (EI): *m/z* (%) 550 (39), 549 (39), 548 (100), 507 (33), 55 (88), 492 (20), 442 (16), 386 (32), 257 (38). HRMS (EI): *m/z* calcd for $C_{35}H_{34}{}^{35}ClN_2P$: 548.2148; found: 548.2137.

1-*N*-Allyl-5-chloro-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5e). Yellow fine crystals, yield 2102 mg (79%), mp 143-146 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.14 (s, 3H), 4.32-4.36 (m, 2H), 4.94-5.03 (dd, *J* 10.5, 1.8 Hz, 1H), 5.35-5.40 (dd, *J* 17.3, 1.8 Hz, 1H), 5.87-5.95 (m, 1H), 6.32 (d, *J* 8.6 Hz, 1H), 6.49-6.51 (m, 2H), 6.72-6.75 (dd, *J* 8.6, 2.6 Hz, 1H), 6.89-6.93 (m, 2H), 7.09 (t, *J* 2.6 Hz, 1H), 7.45-7.49 (m, 6H), 7.51-7.59 (m, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.5, 54.8, 114.0, 115.8, 120.2, 123.2 (d, J_{CP} 11 Hz), 125.1, 125.8, 129.0 (d, J_{CP} 2 Hz), 129.1 (d, J_{CP} 11 Hz), 129.2, 130.4 (d, J_{CP} 99 Hz), 132.4 (d, J_{CP} 3 Hz), 132.5 (d, J_{CP} 10 Hz), 136.0, 141.2 (d, J_{CP} 23 Hz), 146.4, 147.1. MS (EI): *m/z* (%) 534 (37), 532 (79), 427 (43), 401 (17), 386 (37), 378 (44), 278 (44), 269 (26), 262 (100), 243 (36). HRMS (EI): *m/z* calcd for $C_{34}H_{30}{}^{35}ClN_2P$: 532.1835; found: 532.1827.

5-Bromo-1-*N*-butyl-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5f). Yellow oil, yield 2368 mg (80%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.77 (t, *J* 7.3 Hz, 3H), 1.23-1.29 (m, 2H), 1.47-1.54 (m, 2H), 2.14 (s, 3H), 3.63 (t, *J* 7.5H, 2H), 6.29 (d, *J* 8.5 Hz, 1H), 6.47-6.50 (m, 2H), 6.85-6.88 (dd, *J* 8.5 Hz, *J* 2.5 Hz, 1H), 6.90-6.93 (m, 2H), 7.14 (t, *J* 2.5 Hz, 1H), 7.45-7.49 (m, 6H), 7.52-7.58 (m, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 13.9, 19.8, 20.0, 29.7, 50.9, 107.0, 112.9, 123.2 (d, J_{CP} 11 Hz), 123.9, 128.4, 128.7 (d, J_{CP} 12 Hz), 128.8, 129.9 (d, J_{CP} 99 Hz), 131.8 (d, J_{CP} 2 Hz), 132.0 (d, J_{CP} 10 Hz), 132.1, 141.2, 146.3, 147.6. MS (EI): *m/z* (%) 594 (94), 593 (37), 592 (91), 552 (36), 551 (100), 549 (96), 486 (17), 430 (30), 303 (31), 262 (78). HRMS (EI): *m/z* calcd for $C_{35}H_{34}{}^{79}BrN_2P$: 592.1643; found: 592.1640.

1-*N*-Allyl-5-bromo-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5g). Yellow oil, yield 1930 mg (67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.19 (s, 3H),

4.33-4.35 (m, 2H), 5.02-5.06 (m, 1H), 5.31-5.38 (m, 1H), 5.90-6.00 (m, 1H), 6.37 (d, *J* 8.4 Hz, 1H), 6.54-6.58 (m, 2H), 6.82-6.86 (dd, *J* 8.4 Hz, *J* 2.4 Hz, 1H), 6.87-6.90 (m, 2H), 7.28 (t, *J* 2.8 Hz, 1H), 7.33-7.38 (m, 6H), 7.44-7.53 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 54.9, 108.5, 114.2, 115.5, 123.8 (d, J_{CP} 10 Hz), 125.4, 128.5, 128.6 (d, J_{CP} 12 Hz), 129.0, 131.0 (d, J_{CP} 100 Hz), 131.7 (d, J_{CP} 3 Hz), 132.2 (d, J_{CP} 12 Hz), 132.6 (d, J_{CP} 10 Hz), 135.8, 142.2 (d, J_{CP} 22 Hz), 146.6, 147.2. MS (EI): *m/z* (%) 578 (52), 576 (51), 473 (29), 471 (29), 447 (12), 430 (25), 316 (27), 301 (46), 289 (33), 262 (100), 183 (93). HRMS (EI): *m/z* calcd for $C_{34}H_{30}{}^{79}BrN_2P$: 576.1330; found: 576.1326.

1-*N*-Benzyl-5-bromo-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5h). Colourless crystals, yield 2504 mg (80%), mp 164-165 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.12 (s, 3H), 5.00 (s, 2H), 6.28-6.30 (d, *J* 8.5 Hz, 1H), 6.46-6.49 (m, 2H), 6.81-6.84 (dd, *J* 8.5 Hz, *J* 2.5 Hz, 1H), 6.88-6.90 (m, 2H), 7.12-7.14 (m, 3H), 7.30 (t, *J* 2.5 Hz, 1H),7.44-7.48 (m, 6H), 7.51-7.59 (m, 11H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 20.0, 56.2, 107.2, 113.8, 123.2 (d, J_{CP} 11 Hz), 124.9, 126.3, 126.5, 128.0 (d, J_{CP} 10 Hz), 128.7, 128.8 (d, J_{CP} 11 Hz), 129.7 (d, J_{CP} 99 Hz), 130.9, 131.9, 132.0 (d, J_{CP} 10 Hz), 139.8, 141.3, 141.5, 145.9, 146.8. MS(EI): *m/z* (%) 628 (82), 627 (37), 626 (79), 537 (24), 445 (45), 432 (38), 365 (42), 289 (42), 262 (100). HRMS (EI): *m/z* calcd for $C_{38}H_{32}{}^{79}BrN_2P$: 626.1486; found: 626.1494.

1-*N*-Butyl-1-*N*-(4-methylphenyl)-5-phenyl-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (5i).Yellow fine crystals, yield 1151 mg (39%), mp 164-166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (t, *J* 7.1 Hz, 3H), 1.29-1.34 (m, 2H), 1.64-1.69 (m, 2H), 2.20 (s, 3H), 3.69-3.73 (m, 2H), 6.57-6.61 (m, 3H), 6.87-6.92 (m, 2H), 7.08-7.20 (m, 2H), 7.31-7.39 (m, 8H), 7.45-7.51 (m, 6H), 7.56-7.61 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 20.3, 20.5, 30.1, 51.5, 112.9, 122.8 (d, J_{CP} 10 Hz), 123.9, 124.3, 125.7, 126.0, 128.4 (d, J_{CP} 11 Hz), 128.5 (d, J_{CP} 12 Hz), 129.0, 130.2, 131.3 (d, J_{CP} 99 Hz), 131.4, 132.5 (d, J_{CP} 9 Hz), 140.7, 140.9, 141.2, 147.2, 147.9. MS (EI): *m/z* (%) 590 (100), 547 (58), 534 (20), 428 (19), 299 (38), 295 (27), 285 (85), 262 (40), 183 (32). HRMS (EI): *m/z* calcd for $C_{41}H_{39}N_2P$: 590.2851; found: 590.2853.

General procedure for the synthesis of dibenzo[*b*,*e*][1,4]diazepines (6). $POCl_3$ (0.37 mL, 4 mmol) was added dropwise to DMF (0.31 mL, 4 mmol) at ~0 ºC, and the mixture was stirred for 10 min without cooling. A solution of **5** (1 mmol) in dichloroethane (5 mL) was then added dropwise at 25 ºC and the resulting mixture was stirred overnight at 60 ºC. Diluted aqueous K_2CO_3 (2 mL) was added and stirring was continued for 15 min. The mixture was then extracted with EtOAc (3 × 20 mL). The combined organic phases were dried Na_2SO_4 and the solvent was evaporated. The residue was dissolved in toluene (5 mL) and stirred under reflux overnight. The reaction was cooled down to room temperature and the solvent was removed. The residue was separated on column chromatography (SiO_2, hexane/ethyl acetate, 9:1 to 2:1) to obtain pure products **6**.

5-Butyl-7-fluoro-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6a). Yellow oil, yield 195 mg (69%), ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.82 (t, *J* 7.4 Hz, 3H), 1.31-1.37 (m, 2H), 1.44-1.50 (m, 2H), 2.23 (s, 3H), 3.56 (d, *J* 6.9 Hz, 2H), 6.87-6.92 (m, 3H), 7.08-7.12 (m, 2H), 7.24-7.27

(m, 1H), 8.46 (s 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.1, 19.8, 20.4, 29.2, 48.0, 107.7 (d, J_{CF} 24 Hz), 110.9 (d, J_{CF} 22 Hz), 119.4, 129.1 (d, J_{CF} 10 Hz), 129.3, 130.4, 133.0,133.1, 140.1 (d, J_{CF} 3 Hz), 147.9 (d, J_{CF} 9 Hz), 151.6, 162.3 (d, J_{CF} 243 Hz), 162.8. MS(EI): *m/z* (%) 282 (25), 240 (17), 239 (100), 225 (11), 224 (25). HRMS (EI): *m/z* calcd for $C_{18}H_{19}FN_2$: 282.1523; found: 282.1533.

5-Allyl-7-fluoro-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6b).Yellow oil, yield 27 mg (10%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.27 (s, 3H), 4.22 (d, *J* 5.7 Hz, 2H), 5.17-5.19 (dd, *J* 10.3 Hz, *J* 1.5 Hz, 1H), 5.31-5.35 (dd, *J* 17.2 Hz, *J* 1.5 Hz, 1H), 5.75-5.82 (m, 1H),6.57-6.60 (dd, *J* 10.3 Hz, *J* 2.8 Hz, 1H), 6.75-6.78 (m, 2H), 7.00-7.02 (m, 1H), 7.18-7.22 (m, 2H), 8.47 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.4, 51.9, 107.6 (d, J_{CF} 24 Hz), 111.0 (d, J_{CF} 22 Hz), 118.5, 119.3, 128.7, 129.0 (d, J_{CF} 10 Hz), 130.7, 133.0, 133.1, 133.5, 133.7, 147.3 (d, J_{CF} 9 Hz), 151.4, 162.6, 162.8 (d, J_{CF} 246 Hz). MS (EI): *m/z* (%) 266 (33), 226 (20), 225 (100), 210 (17). HRMS (EI): *m/z* calcd for $C_{17}H_{15}FN_2$: 266.1219; found: 266.1221.

5-Butyl-7-chloro-2-methoxy-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6c). Yellow oil, yield 38 mg (12%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* 7.4 Hz, 3H), 1.36-1.42 (m, 2H), 1.54-1.60 (m, 2H), 3.53 (d, *J* 6.9 Hz, 2H), 3.77 (s, 3H), 6.70 (d, *J* 3.0 Hz, 1H), 6.82 (d, *J* 8.9 Hz, 1H), 6.87 (d, *J* 2.3 Hz, 1H), 6.91-6.94 (dd, *J* 8.9 Hz, *J* 3.0 Hz, 1H), 7.00-7.03 (dd, *J* 8.6 Hz, *J* 2.3 Hz, 1H), 7.11 (d, *J* 8.6 Hz, 1H), 8,47 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 20.0, 29.2, 48.7, 55.6, 114.1, 117.8, 119.9, 120.1, 124.0, 129.0, 130.3, 133.3, 142.0, 147.2, 147.5, 155.8, 162.4. MS (EI): *m/z* (%) 316 (18), 315 (11), 314 (52), 273 (45), 271 (100), 228 (15). HRMS (EI): *m/z* calcd for $C_{18}H_{19}{}^{35}ClN_2O$: 314.1186; found: 314.1182.

5-Butyl-7-chloro-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6d). Yellow oil, yield 143 mg (48%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.79 (t, *J* 7.4 Hz, 3H), 1.36-1.42 (m, 2H), 1.55-1.61 (m, 2H), 2.27 (s, 3H), 3.55 (d, *J* 7.1 Hz, 2H), 6.78 (d, *J* 8.3 Hz, 1H), 6.87 (d, *J* 2.1 Hz, 1H), 6.98 (d, *J* 1.8 Hz, 1H), 6.99-7.01 (dd, *J* 8.3 Hz, *J* 2.1 Hz, 1H), 7.09-7.12 (d, *J* 8.0 Hz, 1H), 7.14-7.19 (dd, *J* 8 Hz, *J* 1.8 Hz, 1H), 8.46 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 20.0, 20.4, 29.2, 48.5, 118.8, 120.2, 124.0, 129.0, 129.3, 130.2, 132.6, 133.0, 133.2, 142.2, 147.3, 151.9, 163.2. MS (EI): *m/z* (%) 300 (21), 298 (42), 257 (43), 255 (100), 241 (19), 205 (17). HRMS (EI): *m/z* calcd for $C_{18}H_{19}{}^{35}ClN_2$: 298.1238; found: 298.1237.

5-Allyl-7-chloro-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6e). Yellow oil, yield 71 mg (25%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (s, 3H), 4.22 (d, *J* 5.5 Hz, 2H), 5.15-5.19 (dd, *J* 10.4, 1.4 Hz, 1H), 5.30-5.35 (dd, *J* 17.3, 1.4 Hz, 1H), 5.73-5.82 (m, 1H), 6.75 (d, *J* 8.3 Hz, 1H), 6.83 (d, *J* 2.3 Hz, 1H), 6.97-6.99 (m, 1H), 7.00-7.02 (dd, *J* 8.3, 2.3 Hz, 1H), 7.12 (d, *J* 8.3 Hz, 1H), 7.14-7.17 (dd, *J* 8.3, 1.8 Hz, 1H), 8.48 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.4, 51.8, 118.4, 119.1, 120.4, 124.2, 129.0, 129.2, 130.3, 132.5, 133.1, 133.3, 133.8, 141.9, 146.9, 151.3, 163.2. MS (EI): *m/z* (%) 284 (23), 282 (43), 244 (13), 243 (43), 242 (31), 241 (100), 206 (18), 205 (19). HRMS (EI): *m/z* calcd for $C_{17}H_{15}{}^{35}ClN_2$: 282.0934; found: 282.0932.

7-Bromo-5-butyl-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6f). Yellow oil, yield 237 mg (69%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.80 (t, *J* 7.2 Hz, 3H), 1.28-1.34 (m, 2H), 1.40-1.446 (m, 2H), 2.21 (s, 3H), 3.54-3.56 (m, 2H), 6.91 (d, *J* 8.2 Hz, 1H), 7.0 (d, *J* 8.4 Hz, 1H), 7.11 (d, *J*

1.5 Hz, 1H), 7.15 (d, *J* 2.2 Hz, 1H), 7.19-7.22 (dd, *J* 8.2 Hz, *J* 2.2 Hz, 1H), 7.24-7.26 (dd, *J* 8.4 Hz, *J* 1.5 Hz, 1H), 8.49 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 14.1, 19.8, 20.4, 29.1, 47.9, 119.6, 120.7, 123.4, 127.2, 129.3, 129.5, 130.5, 133.2, 142.9, 148.0, 151.8, 163.9, [one signal invisible]. MS (EI): *m/z* (%) 344 (51), 342 (51), 301 (97), 300 (31), 299 (100), 287 (23), 286 (14), 220 (22), 219 (26), 193 (10). HRMS (EI): *m/z* calcd for $C_{18}H_{19}{}^{79}BrN_2$: 342.0732; found: 342.0746.

5-Allyl-7-bromo-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6g). Yellow oil, yield 108 mg (33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H), 4.22 (d, *J* 5.6 Hz, 2H), 5.15-5.18 (dd, *J* 10.4 Hz, *J* 1.6 Hz, 1H), 5.29-5.34 (dd, *J* 17.2 Hz, *J* 1.6 Hz, 1H), 5.72-5.82 (m, 1H), 6.74 (d, *J* 8.4 Hz, 1H), 6.98 (d, *J* 2.0 Hz, 2H), 7.04 (d, *J* 8.4 Hz, 1H), 7.14-7.17 (dd, *J* 8.4 Hz, *J* 2.0 Hz, 2H), 8.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 51.9, 118.5, 119.2, 121.2, 123.5, 127.3, 129.3, 129.5, 130.4, 132.6, 133.4, 133.9, 142.6, 147.2, 151.5, 163.4. (EI): *m/z* (%) 328 (38), 326 (38), 288 (19), 287 (98), 286 (23), 285 (100), 206 (23), 205 (32). HRMS (EI): *m/z* calcd for $C_{17}H_{15}{}^{79}BrN_2$: 326.0419; found: 326.0425.

5-Benzyl-7-bromo-2-methyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6h). Colourless oil, yield 136 mg (36%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 2.24 (s, 3H), 4.86 (s, 2H), 6.79-6.81 (m, 1H), 6.99-7.24 (m, 3H), 7.42-7.57 (m, 3H), 7.67-7.75 (m, 3H), 8.56 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6, 53.4, 119.2, 121.3, 123.5, 125.6, 127.4, 127.5, 128.1, 128.6, 129.5, 130.5, 132.7, 133.5, 136.8, 142.7, 147.3, 151.5, 163.5. MS (EI): *m/z* (%) 378 (37), 276 (37), 364 (24), 362 (27), 288 (22), 287 (98) 285 (100), 205 (37), 91 (22). HRMS (EI): *m/z* calcd for $C_{21}H_{17}{}^{79}BrN_2$: 376.0575; found: 376.0578.

5-Butyl-2-methyl-7-phenyl-5*H*-dibenzo[*b*,*e*][1,4]diazepine (6i). Yellow oil, yield 136 mg (40%). ^{1}H NMR (500 M Hz, $CDCl_3$): δ 0.89 (t, *J* 7.3 Hz, 3H), 1.40-1.45 (m, 2H), 1.60-1.66 (m, 2H), 2.27 (s, 3H), 3.66 (t, *J* 6.9 Hz, 2H), 6.82 (d, *J* 8.3 Hz, 1H), 7.00 (d, *J* 1.8 Hz, 1H), 7.10 (s, 1H), 7.15-7.18 (dd, *J* 8.2 Hz, *J* 1.8 Hz, 1H), 7.26-7.28 (m, 2H), 7.31-7.35 (m, 1H), 7.40-7.44 (m, 2H), 7.52-7.55 (m, 2H), 8.50 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8, 20.1, 20.4, 29.4, 48.5, 118.6, 118.7, 122.8, 126.9, 127.3, 128.6, 128.7, 129.6, 130.2, 132.5, 132.7, 140.5, 140.7, 142.9, 146.8, 152.5, 162.9. MS (EI): *m/z* (%) 340 (49), 298 (40), 297 (100), 283 (22), 282 (15), 148 (13). HRMS (EI): *m/z* calcd for $C_{24}H_{24}N_2$: 340.1939; found: 340.1938.

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