Quaternization of 2-(arylamino)aryliminophosphoranes. A route to *N*,*N*′-disubstituted 2-aminodiarylamines and unsymmetrically substituted 1-aryl-1,2,5,6-tetrahydro-1,6-benzodiazocines

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Abstract
A convenient route leading to variously substituted *N*-alkyl-*N*′-aryl-*o*-phenylenediamine derivatives via quaternization of the imine nitrogen atom of 2-(arylamino)arylimino-phosphoranes is presented. The method allows to introduce identical or different alkyl groups onto both nitrogen atoms. The *N*,*N*′-bis-allyl derivatives so obtained, after protecting the secondary amine group, easily undergo RCM cyclization providing unsymmetrically substituted 1,2,5,6-tetrahydro-1,6-benzodiazocine systems in high yields.

Keywords: Ring closing metathesis, fused-ring systems, nitrogen heterocycles, nitroso compounds, 1,6-benzodiazocines

Introduction

ortho-Arylenediamines and their N-substituted derivatives belong to the most versatile and useful building blocks in the synthesis of variety of nitrogen heterocyclic structures. Quite often, however, the availability of the appropriately substituted arylenediamines is a problem, their synthesis is difficult, or their stability low. In our laboratory an alternative route from simple nitroarenes and arylamines leading to various fused N-aryl heterocyclic structures has been developed. In 2014 we described a practical synthesis of 2-(arylamino)aryliminophosphoranes from 2-nitrosodiarylamines, easily accessible from the reaction of nitroarenes and anilines.[1] We demonstrated their versatility as N-substituted arylenediamine equivalents in the synthesis of fused bicyclic heterocycles such as benzimidazoles,[2] 2-aminobenzimidazoles,[1] benzotriazoles,[3] benzimidazol-2-ones,[4] benzodiazepines,[2] and benzimidazole-2-thiones.[5]

Their ylide-like structure, a consequence of the charge distribution within the iminophosphorane group, determines the nucleophilic character of the nitrogen atom, which is susceptible to reaction with electrophiles. Among these, condensation with carbonyl compounds,

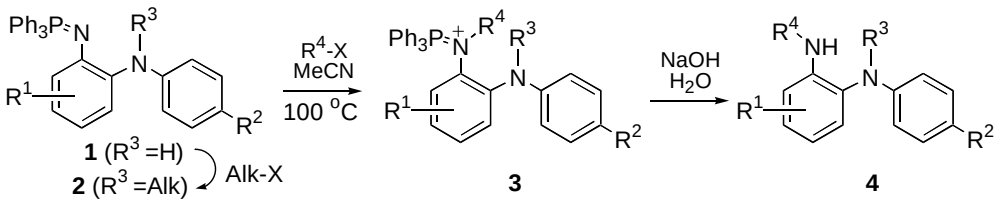
known as the aza-Wittig reaction, seems to be the most common and useful. Simple alkylation of this nitrogen atom, leading to quaternization of the iminophosphorane group, was originally reported in 1964[6] but since then it has been reported only a few times.[7-11] While the reaction has found some attention in the chemistry of non-nucleophilic strong bases,[12] its most practical interest seems to be in the synthesis of mono N-alkylated aryl- and alkylamines.[7-10] The iminophosphorane group can be considered as an amine function protected against dialkylation. There is, however, only one report of the application of such an approach to aromatic amines.

Results and Discussion

In this paper we report the synthesis of *N*-alkyl and *N,N′*-dialkyl *N′*-aryl arylenediamines from 2-(arylamino)aryliminophosphoranes **1**. The latter were synthesized from 2-nitrosodiarylamines by their reaction with excess of PPh_3.[1] The two nitrogen atoms of different nucleophilicity in **1** can be alkylated independently with the same or different alkyl halides. If needed, the diarylamine nitrogen atom was alkylated first, using NaH/DMF or *n*-BuLi/THF systems as has been described earlier.[2] Particular attention was paid to the introduction of allyl substituents on both nitrogen atoms since the resulting structures provide an opportunity for cyclization reactions.

The quaternization was performed in dry MeCN at 100 °C in a sealed ampoule with *ca*. 15 equiv. of the alkyl halide (MeI, AllBr, BnBr) followed by hydrolysis by 15% NaOH in H_2O/dioxane (Scheme 1; Table 1).

The results obtained for the reactions of *N′*-allyliminophosphorane **2c** show that the yields of **4** increase roughly with the reactivity of the alkylating agent (entries 3-7). A similar trend was observed also for the *N′*-butyl derivative **2d** (entries 8 and 9). However, *N′*-unalkylated **1c** reacted poorly with allyl bromide (entry 16). Such an effect of an alkyl group at the diarylamine nitrogen atom is not visible in other comparable examples. Somewhat less active 6-chloro derivatives **2g** (N′-allyl) and **1d** (unsubstituted) gave both very high yields when reacted with allyl bromide (entries 19 and 11). Almost equal yields were obtained also in other pairs which differ only with the substitution on the *N′* atom (cf. entries 11 and 17, or 12 and 22). In general, a positive outcome of the reaction depends on the reactivity of both reagents so that weakly nucleophilic diamines react poorly or do not enter the reaction at all, even with MeI, the most reactive alkylating agent used (entry 26). On the other hand, MeI reacted with some diamines **4** unselectively, giving complex mixtures of products (entries 15 and 28).



Scheme 1. Synthesis of *N*-monoalkylated *N'*-aryl-*o*-arylenediamines **4**.

Table 1. Synthesis of *N*-alkyl-2-alkylaminodiarylamines **4** from aryliminophosphoranes **1**

Entry	R^1	R^2	**1**	*N'*-Alkylation			Quaternization/hydrolysis				
				R^3	**2**	Yield[a] (%)	R^4	X	Time (h)	**4**	Yield[a] (%)
1	4-Cl	Cl	**1a**	Bu	**2a**	80	Me	I	24	**4a**	79
2	4-Br	Me	**1b**	Bn	**2b**[b]	80	Me	I	24	**4b**	44
3							methallyl	Cl[d]	24	**4c**	50
4							Me	I	3	**4d**	87
5	4-OMe	Me	**1c**	allyl	**2c**	99	Bu	I	24	**4e**	46
6							Bn	Br	5	**4f**	61[c]
7							allyl	Br	24	**4g**	69
8	4-OMe	Me	**1c**	Bu	**2d**	99	Me	I	3	**4h**	81
9							allyl	Br	48	**4i**	71
10	4-OMe-6-Cl	Cl	**1d**	H	**-**	**-**	allyl	Br	24	**4j**	81
11	4-OMe	Cl	**1e**	H	**-**	-	allyl	Br	5	**4k**	78
12	4-F	Cl	**1f**	H	**-**	-	allyl	Br	24	**4l**	72
13	4-Cl-6-OMe	OEt	**1g**	H	**-**	-	allyl	Br	24	**4m**	70
14	4-Cl	Cl	**1a**	H	**-**	-	allyl	Br	24	**4n**	70
15	4-OMe	Me	**1c**	H	**-**	-	Me	I	24		f
16							allyl	Br	48	**4o**	35
17	4-OMe	Cl	**1e**	allyl	**2e**	96	allyl	Br	4	**4p**	78
18	4-OMe	OEt	**1h**	allyl	**2f**	74	allyl	Br	24	**4q**	64
19	4-OMe-6-Cl	Cl	**1d**	allyl	**2g**	76	allyl	Br	24	**4r**	87
20	H	H	**1b**	allyl	**2h**	97	allyl	Br	4.5	**4s**	82
21	4-F	Me	**1i**	allyl	**2i**[b]	88	allyl	Br	24	**4t**	74
22	4-F	Cl	**1f**	Bu	**2j**[g]	53	allyl	Br	24	**4u**	73
23	4-Cl	Me	**1j**	allyl	**2k**[b]	79	allyl	Br	24	**4v**	48
24	4,6-Cl_2	Cl	**1k**	H	**-**	-	allyl	Br	5	**4w**	85
25	4,6-Cl_2	Cl	**1k**	allyl	**2l**	86	allyl	Br	16	**4x**	25
26	4,6-Cl_2	CN	**1l**	Bu	**2m**	83	Me	I	120		e
27							allyl	Br	24		e
28	H	H	**1b**	H	**-**	-	allyl	Br	24		f
29	4-OMe	Me	**1c**	2-methylallyl	**2n**	74	-	-	-	-	-
30	4-OMe	Me	**1c**	propargyl	**2o**	98	allyl	Br	4	**4y**	77

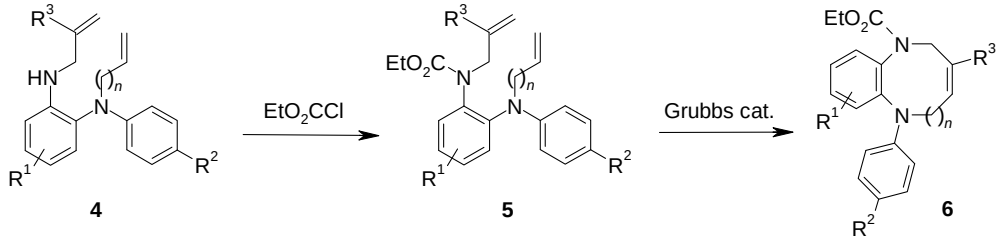
Table 1. Continued

Entry	R^1	R^2	**1**	*N'*-Alkylation			Quaternization/hydrolysis				
				R^3	**2**	Yield[a] (%)	R^4	X	Time (h)	**4**	Yield[a] (%)
31	4-OMe	Me	**1c**	pent-4-enyl	**2p**	58	allyl	Br	3	**4z**	76
32	4-OMe	Me	**1c**	hex-5-enyl	**2q**	61	allyl	Br	4	**4za**	79

[a] Isolated yield. [b] Ref. 2. [c] 1.1 equiv. of BnBr was used. [d] With KI as catalyst. [e] No reaction. [f] Complex mixture. [g] Ref. 3.

The most interesting 2-aminoarylenediamines **4** are those carrying allylic groups at both nitrogen atoms. It is then possible to perform a ring closing metathesis cyclization (RCM) providing a fused eight-membered ring containing nitrogen. The RCM reaction has become a popular method to synthesize medium-sized rings and many synthetic applications of RCM for benzannulation leading to fused nitrogen heterocyclic systems have been observed in recent years.[13-22] A separate problem seems to be the synthesis of suitable starting materials.

The methodology presented in this paper offers a simple and efficient way to prepare *N*,*N*′-diallyl *ortho*-arylenediamines **4**, designed for the RCM heteroannulation providing 1,6-benzodiazocine derivatives. The entire synthetic pathway starts from *N*-aryl-2-nitrosoanilines as precursors of **1**: thus, one of the nitrogen atoms does carry an aryl substituent. This attribute makes it possible to synthesize a novel class of 1,6-benzodiazocine systems, N,N′-substituted unsymmetrically, with an aryl ring at one of the nitrogen atoms. To our best knowledge, no synthesis of such compounds has been reported so far. Thus, it was decided to verify the efficacy of the approach, employing the reputable and commercially available Grubbs catalysts.[22,23] As expected, an unprotected NH group in **4** effectively deactivate the catalysts and the reaction did not proceed within a reasonable time. An attempt to apply the existing iminophosphorane group as a protecting group: *i.e.* to perform the metathesis reaction with crude salts **3** ($R^3 = R^4$ = allyl in Table 1) also failed. Amongst other common protecting methods, the reaction of **4** with ethyl chloroformate forming carbamates **5** appeared to be the most efficient (Scheme 2 and Table 2).



Scheme 2. Synthesis of tetrahydro-1,6-benzodiazocines **6**.

Table 2. Synthesis and ring closing metathesis of **5**

Entry	*N*-Acylation							Ring closing metathesis			
	4	R^1	R^2	R^3	*n*	**5**	Yield [a] (%)	Grubbs catalyst[b]	Time (h)	**6**	Yield [a] (%)
1	**4g**	4-OMe	Me	H	1	**5a**	88	I (5 mol%)	5	**6a**	81
2	**4q**	4-OMe	OEt	H	1	**5b**	83	I (5 mol%)	5	**6b**	96
3	**4r**	4-OMe-6-Cl	Cl	H	1	**5c**	82	I (5 mol%)	2	**6c**	84
4	**4s**	H	H	H	1	**5d**	94	I (5 mol%)	5	**6d**	87
5	**4t**	4-F	Me	H	1	**5e**	95	II (4 mol%)	0.5	**6e**	98
6								I (5 mol%)	4.5	**6e**	90
7	**4c**	4-OMe	Me	Me	1	**5f**	83	II (5 mol%)	2	**6f**	90
8	**4z**	4-OMe	Me	H	3	**5g**	97	I (5 mol%)	24	**6g**	43[c]

[a] Isolated yield. [b] I = benzylidene-bis(tricyclohexylphosphine)-dichlororuthenium, II = [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene) (tricyclohexylphosphine)ruthenium. [c] A mixture of *E* and *Z* isomers.

The protected diamines **5** were subjected to ring closing metathesis cyclization with the first (I) and the second (II) generation of Grubbs catalysts, the newer one being somewhat more efficient than the older. Nevertheless, even when using the first generation catalyst the yields were very good for all starting *bis*-allylated diamines, regardless of substituents in the aryl rings. The structures of the products were unambiguously determined; the *Z*-configuration of the double bond was proved by homo-decoupling technique which revealed a J_{HH} = 10.8 Hz for the vinylic protons. It is noteworthy that isomerization, *i.e.* migration of the double bond, reported as associated with the methodology,[18-20,24,25] possibly prior to or after the cyclization, did not take place.

Attempts to close larger rings from *N′*-pent-4-enyl and *N′*-hex-5-enyl derivatives (**4z** and **4za** respectively) were successful only in the former case. Iminophosphorane **4z** was obtained, protected with ethyl chloroformate, and cyclized using the Grubbs I catalyst providing 10-membered ring derivative **6g** in moderate yield, as an inseparable mixture of *E* and *Z* isomers. Unfortunately, from the obtained NMR spectra it was not possible to determine the precise constitution of the mixture. In the case of **4za** a complex mixture of products was produced under the normal RCM conditions.

Conclusions

Quaternization of the imine nitrogen atom of 2-(arylamino)aryliminophosphoranes provides a convenient route to diversely substituted *N*-alkyl-*N′*-aryl-*o*-phenylenediamine derivatives. The

starting iminophosphoranes are accessible in a two-step procedure from simple nitroarenes and arylamines through 2-nitrosodiarylamines.[1] The method allows introduction of identical or different alkyl groups onto both nitrogen atoms, thus providing useful starting materials for the synthesis of various fused heterocyclic systems. As an example, N,N′-diallyl derivatives obtained this way, after protection of the secondary amine group, were subjected to RCM cyclization providing unsymmetrically substituted 1,2,5,6-tetrahydro-1,6-benzodiazocine systems in high yields.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 400 MHz or on Varian VNMRS 600 MHz and VNMRS 500 MHz instruments at 298 K, unless specified otherwise. Chemical shifts are expressed in ppm referred to TMS (^{1}H NMR) or to the solvent used (^{13}C NMR), with coupling constants in Hertz. Mass spectra were obtained on a AutoSpec Premier (Waters) spectrometer (EI, 70 eV) or on a 4000 Q-TRAP (Applied Biosystems) (ESI). Silica gel Merck 60 (230-400 mesh) was used for column chromatography. THF was distilled from sodium/benzophenone ketyl prior to use. Common reagents and materials were purchased from commercial sources and used as received. Preparation and characterization of 2-(arylamino)aryliminophosphoranes **1a-c**,**f**,**g**,**i**,**j**,**l**, **2b** and **2i-k** have been described in our previous papers.[1-3]

General procedure for the synthesis of new iminophosphoranes 1. To a stirred suspension of Ph_3P (12.5 mmol, 3280 mg) in dry MeCN (25 mL) the appropriate *N*-aryl-2-nitrosoaniline (5 mmol) was added portionwise during 30 min under external cooling with cold water. The mixture was stirred at r.t. overnight. The precipitated fine crystals was filtered off, the filtrate was concentrated under vacuum and the residue was chromatographed using hexane-EtOAc gradient elution (9:1 to 2:1). An analytically pure sample of the product was obtained by recrystallization from EtOAc-hexane.

3-Chloro-1-*N*-(4-chlorophenyl)-5-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (1d). Fine colourless crystals (2466 mg, 91%), mp 137-139 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.60 (s, 3H), 6.32-6.34 (m, 1H), 6.59-6.61 (m, 1H), 6.77-6.80 (m, 2H), 6.99 (s, 1H), 7.14-7.17 (m, 2H), 4.49-7.51 (m, 6H), 7.55-7.57 (m, 3H), 7.61-7.65 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 55.1, 100.5, 105.4, 117.9, 123.0, 128.1 (d, J_{CP} 8 Hz), 128.6, 128.7 (d, J_{CP} 13 Hz), 130.8, 131.6, 131.7 (d, J_{CP} 100 Hz), 131.8 (d, J_{CP} 9 Hz), 139.1 (d, J_{CP} 9 Hz), 141.7, 151.7 (d, J_{CP} 3 Hz). MS (EI): *m/z* (%) 544 (77), 543 (49), 542 [M$^+$] (47), 263 (25), 262 (76), 236 (11); HRMS (EI): Calcd for $C_{31}H_{25}{}^{35}Cl_2N_2PO$: 542.1082; found: 542.1081.

1-*N*-(4-Chlorophenyl)-5-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (1e). Fine yellow crystals (2362 mg, 93%), mp 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 3H), 6.03-6.06 (m, 1H), 6.37-6.40 (m, 1H), 6.85-6.87 (m, 1H), 7.10-7.13 (m, 2H), 7.17-7.20

(m, 2H), 7.42-7.46 (m, 6H), 7.49-7.54 (m, 4H), 7.69-7.74 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 100.8, 103.5, 119.2, 119.9 (d, J_{CP} 9 Hz), 124.6, 128.8 (d, J_{CP} 12 Hz), 129.1, 131.3 (d, J_{CP} 99 Hz), 131.9 (d, J_{CP} 3 Hz), 132.6 (d, J_{CP} 10 Hz), 132.8, 138.1 (d, J_{CP} 19 Hz), 142.5, 152.4; MS (EI): *m/z* (%) 510 (36), 508 [M^+] (100), 493 (15), 262 (52), 262 (84), 183 (47); HRMS (EI): Calcd for $C_{31}H_{26}{}^{35}ClN_2PO$: 508.1471; found: 508.1460.

2-*N*-(4-Ethoxyphenyl)-4-methoxy-1-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (1h). Fine yellow crystals (2279 mg, 88%), mp 123-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (t, *J* 8.0 Hz, 3H), 3.64 (s, 3H), 3.98-4.05 (m, 2H), 5.94-5.96 (m, 1H), 6.34-6.36 (m, 1H), 6.71 (s, 1H), 6.83-6.85 (m, 2H), 7.15-7.24 (m, 3H), 7.44-7.51 (m, 9H), 7.72-7.76 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 55.5, 64.0, 99.0, 101.7, 115.4, 119.4 (d, J_{CP} 12 Hz), 122.1, 128.7 (d, J_{CP} 11 Hz), 131.5 (d, J_{CP} 99 Hz), 131.7, 131.8 (d, J_{CP} 2 Hz), 132.7 (d, J_{CP} 9 Hz), 136.9, 140.5 (d, J_{CP} 22 Hz), 152.7, 154.0; MS (EI): *m/z* (%) 518 [M^+] (100), 490 (17), 262 (37), 199 (14), 183 (28); HRMS (EI): Calcd for $C_{33}H_{31}N_2PO_2$: 518.2123; found: 518.2108.

3,5-Dichloro-1-*N*-(4-chlorophenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (1k). Fine colorless crystals (2675 mg, 98%), mp 152-155 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.72-6.84 (m, 3H), 6.90-6.98 (m, 1H), 7.06-7.10 (m, 1H), 7.12-7.22 (m, 2H), 7.44-7.70 (m, 15H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 112.2 (d, J_{CP} 3 Hz), 118.5, 119.5, 121.5, 123.8, 127.8 (d, J_{CP} 8 Hz), 128.3 (d, J_{CP} 11 Hz), 128.6, 131.2, (d, J_{CP} 102 Hz), 131.3 131.4, 136.2, 139.8 (d, J_{CP} 9 Hz), 141.0; MS (EI): *m/z* (%) 548 (100), 547 (56), 546 [M^+] (99), 511 (10), 296 (15), 262 (84); HRMS (EI): Calcd for $C_{30}H_{22}{}^{35}Cl_3N_2P$: 546.0586; found: 546.0589.

General procedure for *N′*-alkylation of iminophosphoranes 1. 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. The cooling bath was removed and the reaction mixture was stirred at r.t. for 24 h. The reaction mixture was then poured into water and extracted with EtOAc. The combined organic phases were dried with Na_2SO_4. After evaporation, the crude product was subjected to column chromatography (hexane/ethyl acetate, 9:1 to 2:1). Solid products were recrystallized from hexane/ethyl acetate mixture.

1-*N*-Butyl-5-chloro-1-*N*-(4-chlorophenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2a). Fine colorless crystals crystals (2344 mg, 80%), mp 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (t, *J* 7.2 Hz, 3 H), 1.25-1.35 (m, 2 H), 1.54-1.65 (m, 2 H), 3.58-3.64 (m, 2 H), 6.41-6.52 (m, 3 H), 6.73-6.79 (m, 1 H), 6.95-7.02 (m, 2 H), 7.07-7.10 (m, 1 H), 7.32-7.41 (m, 6 H), 7.44-7.55 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.5, 30.1, 52.0, 114.3, 120.3, 121.4, 123.3 (d, J_{CP} 11 Hz), 126.4, 128.3, 128.6 (d, J_{CP} 12 Hz), 130.1, 130.9 (d, J_{CP} 99 Hz), 131.7 (d, J_{CP} 3 Hz), 132.5 (d, J_{CP} 10 Hz), 140.8 (d, J_{CP} 22 Hz), 147.2, 147.7. MS (EI): *m/z* (%) 570 [M^+] (47), 568 (67), 527 (70), 512 (17), 386 (43), 262 (100); HRMS (EI): Calcd for $C_{34}H_{31}{}^{35}Cl_2N_2P$: 568.1602, found: 568.1607.

1-*N*-Allyl-5-methoxy-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2c). Fine yellow crystals (2631 mg, 99%), mp 103-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.30 (s, 3 H), 3.66 (s, 3 H), 4.30-4.35 (m, 2 H), 5.00-5.06 (m, 1 H), 5.30-5.37 (m, 1

H), 5.90-6.02 (m, 1 H), 6.40-6.44 (m, 1 H), 6.48-6.58 (m, 3 H), 6.78-6.82 (m, 1 H), 6.84-6.89 (m, 2 H), 7.30-7.37 (m, 6 H), 7.43-7.48 (m, 3 H), 7.50-7.56 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 54.7, 55.7, 111.5, 114.1, 115.2, 115.4, 123.2, 125.0, 128.4 (d, J_{CP} 12 Hz), 128.8 (d, J_{CP} 12 Hz), 129.0, 131.8 (d, J_{CP} 98 Hz), 132.7 (d, J_{CP} 11 Hz), 136.2, 141.1, 141.4, 146.8, 152.1. MS (EI): *m/z* (%) 528 [M^+] (100), 488 (18), 423 (43), 382 (27), 278 (33); HRMS (EI): Calcd for $C_{35}H_{33}N_2OP$: 528.2331, found: 528.2305.

1-*N*-Butyl-5-methoxy-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2d). Fine colorless crystals (2693 mg, 99%), mp 134-137 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.77 (t, *J* 8.0 Hz, 3 H), 1.22-1.30 (m, 2 H), 1.47-1.55 (m, 2 H), 2.13 (s, 3 H), 3.54-3.67 (m, 5 H), 6.31-6.40 (m, 2 H), 6.44-6.50 (m, 2 H), 6.60-6.65 (m, 1 H), 6.84-6.91 (m, 2 H), 7.39-7.61 (m, 15 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.4, 20.3, 20.5, 30.2, 51.2, 55.6, 111.8, 113.1, 116.3, 122.3 (d, J_{CP} 11 Hz), 123.8, 128.9 (d, J_{CP} 12 Hz), 129.2, 131.4 (d, J_{CP} 99 Hz), 132.0, 132.5 (d, J_{CP} 9 Hz), 140.0, 141.8, 147.2, 151.7. MS (EI): *m/z* (%) 544 [M^+] (100), 501 (59), 488 (30), 382 (30), 262 (33); HRMS (EI): Calcd for $C_{36}H_{37}N_2OP$: 544.2644; found: 544.2639.

1-*N*-Allyl-1-*N*-(4-chlorophenyl)-5-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2e). Fine yellow crystals (2614 mg, 96%), mp 95-98 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.59 (s, 3 H), 4.30-4.35 (m, 2 H), 5.00-5.05 (m, 1 H), 5.41-5.46 (m, 1 H), 5.88-5.93 (m, 1 H), 6.31-6.35 (m, 2 H), 6.52-6.56 (m, 2 H), 6.72-6.75 (m, 1 H), 7.05-7.09 (m, 2 H), 7.44-7.55 (m, 15 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 55.2, 55.6, 112.3, 115.0, 115.4, 115.9, 119.6, 122.3, 128.3, 129.1 (d, J_{CP} 12 Hz), 131.0 (d, J_{CP} 99 Hz), 132.2, 132.4 (d, J_{CP} 10 Hz), 135.5, 139.5 (d, J_{CP} 23 Hz), 141.2, 147.8, 151.8. MS (EI): *m/z* (%) 550 (45), 549 (48), 548 [M^+] (100), 508 (13), 397 (29), 278 (42), 271 (67): HRMS (EI): Calcd for $C_{34}H_{30}{}^{35}ClN_2PO$: 548.1784, found: 548.1771.

1-*N*-Allyl-1-*N*-(4-ethoxyphenyl)-5-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2f). Fine yellow crystals (2065 mg, 74%), mp 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (t, *J* 8.0 Hz, 3 H), 3.66 (s, 3 H), 3.88-3.95 (m, 2 H), 4.32-4.35 (m, 2 H), 5.02-5.05 (m, 1 H), 5.32-5.38 (m, 1 H), 5.92-6.02 (m, 1 H), 6.38-6.41 (m, 1 H), 6.49-6.52 (m, 1 H), 6.55-6.60 (m, 2 H), 6.65-6.68 (m, 2 H), 6.77-6.80 (m, 1 H), 7.32-7.38 (m, 6 H), 7.42-7.48 (m, 3 H), 7.50-7.57 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 55.1, 55.7, 64.4, 111.2, 115.0, 115.2, 115.3, 115.4, 123.2 (d, J_{CP} 9 Hz), 128.4 (d, J_{CP} 11 Hz), 131.4 (d, J_{CP} 3 Hz), 131.8 (d, J_{CP} 99 Hz), 132.7 (d, J_{CP} 9 Hz), 136.4, 141.1, 141.6 (d, J_{CP} 21 Hz), 143.6, 150.5, 152.1. MS (EI): *m/z* (%) 558 [M^+] (100), 518 (88), 453 (39), 382 (29), 281 (87); HRMS (EI): Calcd for $C_{36}H_{35}N_2PO_2$: 558.2436, found: 558.2452.

1-*N*-Allyl-3-chloro-1-*N*-(4-chlorophenyl)-5-methoxy-2-*N*-(triphenyl-λ^5-phosphanylidene)-benzene-1,2-diamine (2g). Fine colorless crystals (2225 mg, 76%), mp 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64-3.67 (m, 5 H), 5.00-5.02 (m, 1 H), 5.04-5.07 (m, 1 H), 5.69-5.80 (m, 1 H), 6.23-6.28 (m, 2 H), 6.56-6.58 (m, 1 H), 6.84-6.86 (m, 1 H), 6.87-6.91 (m, 2 H), 7.29-7.33 (m, 6 H), 7.41-7.47 (m, 3 H), 7.48-7.53 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.7, 55.8, 113.8, 114.8, 114.9, 116.8, 121.1, 128.2 (d, J_{CP} 12 Hz), 128.4, 131.2 (d, J_{CP} 13 Hz), 131.4 (d, J_{CP}

9 Hz), 132.7 (d, J_{CP} 10 Hz), 132.9 (d, J_{CP} 102 Hz), 134.1, 138.8, 141.8 (d, J_{CP} 9 Hz), 147.0, 151.9 (d, J_{CP} 2 Hz). MS (EI): *m/z* (%) 584 (32), 582 [M^+] (44), 477 (24), 416 (37), 305 (47), 293 (47), 278 (100); HRMS (EI): Calcd for $C_{34}H_{29}{}^{35}Cl_2N_2PO$: 582.1395; found: 582.1386.

1-*N*-Allyl-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2h). Fine colorless crystals (2344 mg, 97%), mp 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.35-4.41 (m, 2 H), 5.00-5.07 (m, 1 H), 5.34-5.42 (m, 1 H), 5.93-6.05 (m, 1 H), 6.54-6.68 (m, 5 H), 6.77-6.83 (m, 1 H), 7.02-7.09 (m, 2 H), 7.15-7.20 (m, 1 H), 7.30-7.38 (m, 6 H), 7.41-7.47 (m, 3 H), 7.50-7.58 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.1, 113.5, 115.3, 115.7, 117.8, 123.0 (d, J_{CP} 10 Hz), 126.3, 128.5 (d, J_{CP} 12 Hz), 130.1, 131.4 (d, J_{CP} 99 Hz), 131.5 (d, J_{CP} 2 Hz), 132.7 (d, J_{CP} 10 Hz), 136.1, 140.4, 140.7, 148.2, 149.4. MS (EI): *m/z* (%) 484 [M^+] (63), 444 (35), 379 (58), 278 (26), 262 (100), 222 (46); HRMS (EI): Calcd for $C_{33}H_{29}N_2P$: 484.2073, found: 484.2068.

1-*N*-Allyl-1-*N*-(4-chlorophenyl)-3,5-dichloro-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2l). Fine yellow crystals (2520 mg, 86%), mp 100-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63-3.68 (m, 2 H), 5.00-5.07 (m, 2 H), 5.70-5.77 (m, 1 H), 6.24-6.28 (m, 2 H), 6.90-6.96 (m, 3 H), 7.21-7.53 (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.8, 115.0, 117.1, 121.6, 122.2, 127.7, 128.3 (d, J_{CP} 12 Hz), 128.5, 128.8, 131.3, 131.5, 132.6 (d, J_{CP} 104 Hz), 132.7 (d, J_{CP} 10 Hz), 133.7, 142.3, 144.4, 146.9. MS (EI): *m/z* (%) 588 (36), 586 [M^+] (20), 483 (17), 481 (18), 278 (100), 262 (99); HRMS (EI): Calcd for $C_{33}H_{26}{}^{35}Cl_3N_2P$: 586.0899, found: 586.0884.

1-*N*-Butyl-1-*N*-(4-cyanophenyl)-3,5-dichloro-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2m). Fine yellow crystals (2461 mg, 83%), mp 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, *J* 8.0 Hz, 3 H), 1.15-1.25 (m, 2 H), 1.42-1.55 (m, 2 H), 3.20-3.25 (m, 2 H), 6.29-6.33 (m, 2 H), 6.92-6.94 (m, 2 H), 7.18-7.22 (m, 2 H), 7.24-7.26 (m, 1 H), 7.30-7.36 (m, 6 H), 7.42-7.49 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.2, 28.7, 50.4, 97.4, 112.6, 121.0, 122.1 (d, J_{CP} 2 Hz), 128.4 (d, J_{CP} 13 Hz), 128.5, 128.9, 131.0 (d, J_{CP} 7 Hz), 131.5 (d, J_{CP} 3 Hz), 132.4 (d, J_{CP} 10 Hz), 132.5 (d, J_{CP} 104 Hz), 133.2, 140.5 (d, J_{CP} 12 Hz), 144.4, 151.4. MS (EI): *m/z* (%) 595 (32), 593 [M^+] (44), 552 (41), 549 (54), 422 (24), 262 (100); HRMS (EI): Calcd for $C_{35}H_{30}{}^{35}ClN_3P$: 593.1554, found: 593.1557.

5-Methoxy-1-*N*-(4-methylphenyl)-1-*N*-(2-methyl-2-propenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)benzene-1,2-diamine (2n). Yellow oil (2005 mg, 74%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.71 (s, 3 H), 2.19 (s, 3 H), 3.67 (s, 3 H), 4.08-4.14 (m, 2 H), 4.78 (s, 1 H), 5.24 (s, 1 H), 6.39-6.56 (m, 4 H), 6.84-6.86 (m, 3 H), 7.31-7.53 (m, 15 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.4, 20.5, 55.7, 58.9, 110.4, 111.3, 113.9, 115.3, 123.0 (d, J_{CP} 10 Hz), 124.8, 128.4 (d, J_{CP} 12 Hz), 128.9, 131.4 (d, J_{CP} 2 Hz), 131.8 (d, J_{CP} 99 Hz), 132.7 (d, J_{CP} 9 Hz), 141.1, 141.4 (d, J_{CP} 20 Hz), 142.6, 147.1, 152.0. MS (EI): *m/z* (%) 542 (100), 488 (15), 397 (26), 265 (44), 239 (41), 183 (47); HRMS (EI): Calcd for $C_{36}H_{35}N_2PO$: 542.2487; found: 542.2465.

5-Methoxy-1-*N*-(4-methylphenyl)-1-*N*-(2-propynyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)-benzene-1,2-diamine (2o). Fine yellow crystals (2572 mg, 98%), mp 149-152 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.10-2.14 (m, 1 H), 2.23 (s, 3 H), 3.65 (s, 3 H), 4.42-4.45 (m, 2 H), 6.42-6.45 (m, 1 H), 6.53-6.56 (m, 1 H), 6.68-6.70 (m, 2 H), 6.87-6.89 (m, 1 H), 6.92-6.94 (m, 2 H), 7.33-7.37 (m, 6 H), 7.43-7.48 (m, 3 H), 7.54-7.60 (m, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ

20.5, 40.5, 55.7, 71.3, 81.9, 111.9, 114.1, 115.3, 123.7 (d, J_{CP} 10 Hz), 126.5, 128.5 (d, J_{CP} 12 Hz), 129.1, 131.5 (d, J_{CP} 3 Hz), 131.8 (d, J_{CP} 99 Hz), 132.7 (d, J_{CP} 9 Hz), 140.6, 141.1 (d, J_{CP} 19 Hz), 145.9, 152.3. MS (EI): *m/z* (%) 526 (6), 341 (20), 264 (100), 249 (26), 183 (32), 108 (18); HRMS (EI): Calcd for $C_{35}H_{31}N_2PO$: 526.2174; found: 526.2181.

5-Methoxy-1-*N*-(4-methylphenyl)-1-*N*-(pent-4-enyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)-benzene-1,2-diamine (2p). Yellow oil (1612 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.78 (m, 2 H), 2.00-2.07 (m, 2 H), 2.19 (s, 3 H), 3.64-3.69 (m, 5 H), 4.84-4.93 (m, 2 H), 5.69-5.80 (m, 1 H), 6.41-6.44 (m, 1 H), 6.49-6.53 (m, 3 H), 6.73-6.76 (m, 1 H), 6.86-6.89 (m, 2 H), 7.31-7.35 (m, 6 H), 7.42-7.46 (m, 3 H), 7.51-7.56 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 27.1, 31.6, 51.2, 55.8, 111.7, 113.4, 114.5, 115.9, 123.1 (d, J_{CP} 10 Hz), 124.4, 128.4 (d, J_{CP} 8 Hz), 129.1, 131.3 (d, J_{CP} 3 Hz), 131.9 (d, J_{CP} 99 Hz), 132.7 (d, J_{CP} 10 Hz), 138.9, 140.9 (d, J_{CP} 21 Hz), 141.7, 147.0, 152.1. MS (EI): *m/z* (%) 556 (56), 515 (20), 488 (13), 278 (17), 253 (100), 239 (30), 224 (10), 183 (29), 108 (17); HRMS (EI): Calcd for $C_{37}H_{37}N_2PO$: 556.2644; found: 556.2642.

1-*N*-(Hex-5-enyl)-5-methoxy-1-*N*-(4-methylphenyl)-2-*N*-(triphenyl-λ^5-phosphanylidene)-benzene-1,2-diamine (2q). Yellow oil (1739 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33-1.41 (m, 2 H), 1.60-1.70 (m, 2 H), 1.94-2.00 (m, 2 H), 2.19 (s, 3 H), 3.62-3.71 (m, 5 H), 4.84-4.93 (m, 2 H), 5.67-5.77 (m, 1 H), 6.41-6.44 (m, 1 H), 6.49-6.52 (m, 3 H), 6.74-6.76 (m, 1 H), 6.84-6.88 (m, 2 H), 7.31-7.36 (m, 6 H), 7.42-7.47 (m, 3 H), 7.50-7.56 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 26.8, 27.5, 33.9, 51.5, 55.8, 111.7, 113.4, 114.3, 115.9, 123.1 (d, J_{CP} 10 Hz), 124.3, 128.4 (d, J_{CP} 12 Hz), 129.1, 131.3 (d, J_{CP} 3 Hz), 131.9 (d, J_{CP} 99 Hz), 132.7 (d, J_{CP} 10 Hz), 139.1, 141.2, 141.7, 147.0, 152.1. MS (EI): *m/z* (%) 570 (100), 501 (56), 488 (42), 464 (21), 383 (34), 262 (44), 183 (47); HRMS (EI): Calcd for $C_{38}H_{39}N_2PO$: 570.2800; found: 570.2773.

General procedures for the synthesis of 2-(alkylamino)diarylamines 4. A solution of **1** or **2** (1 mmol) in dry MeCN (10 mL) was placed in a glass ampoule equipped with a teflon stopcock, and appropriate alkyl halide (15 mmol) was added in one portion. The reaction flask was tightened and the mixture was stirred at 100 °C for the time specified in Table 1. After the reaction was complete the solvent was evaporated. To the residue was added dioxane (5 mL) and 15% aqueous NaOH (1 mL) and the mixture was stirred at r.t. for 1 h, then poured into water and extracted with Et_2O. The organic phase was dried over Na_2SO_4. After evaporation, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate, 9:1 to 2:1).

***N*-Butyl-4,5′-dichloro-2′-(methylamino)diphenylamine (4a)**. Yellow oil (257 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* 7.0 Hz, 3H), 1.28-1.38 (m, 2H), 1.56-1.64 (m, 2H), 2.78 (s, 3H), 3.42-3.50 (m, 2H), 4.07 (br s, 1H), 6.46-6.51 (m, 2H), 6.62 (d, *J* 8.0 Hz, 1H), 6.97 (d, *J* 4.0 Hz, 1H), 7.08-7.13 (m, 2H), 7.15-7.18 (dd, *J* 8.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.4, 29.6, 30.5, 51.2, 111.6, 114.8, 121.2, 122.7, 128.0, 129.0, 129.1, 132.5, 145.4, 146.6. MS (EI): *m/z* (%) 324 (71), 323 (33), 322 [M^+] (100), 279 (70), 244 (29), 215 (29); HRMS (EI): Calcd for $C_{17}H_{20}{}^{35}Cl_2N_2$: 322.1004, found: 322.1006.

***N*-Benzyl-5-bromo-4′-methyl-2-(methylamino)diphenylamine (4b)**. Yellow oil (168 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.70 (s, 3H), 4.13 (br s, 1H), 4.70-4.76 (m, 2H), 6.51-6.58 (m, 3H), 6.93-6.99 (m, 2H), 7.19-7.32 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 30.5, 56.2, 108.0, 112.2, 114.6, 127.1, 127.2, 128.0, 128.7, 129.8, 130.5, 131.4, 134.5, 138.9, 145.7, 145.8. MS (EI): *m/z* (%) 382 (69), 380 [M^+] (70), 291 (91), 289 (100), 261 (34); HRMS (EI): Calcd for $C_{21}H_{21}{}^{79}BrN_2$: 380.0888; found: 380.0889.

***N*-Allyl-4′-methyl-2-[(2-methylpropenyl)amino]-5-methoxydiphenylamine (4c)**. Yellow oil (160 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 3H), 2.14 (s, 3H), 3.51-3.55 (m, 2H), 3.62 (s, 3H), 4.07-4.10 (m, 2H), 4.71-4.81 (m, 2H), 4.89 (br s, 1H), 5.05-5.12 (m, 1H), 5.15-5.21 (m, 1H), 5.85-5.97 (m, 1H), 6.48-6.55 (m, 3H), 6.60-6.63 (m, 1H), 6.65-6.69 (m, 1H), 6.88-6.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 20.5, 50.2, 54.1, 56.0, 110.7, 112.2, 113.0, 114.5, 115.1, 117.0, 127.2, 129.7, 133.7, 134.9, 139.9, 143.1, 145.9, 151.8. MS (EI): *m/z* (%) 322 [M^+] (94), 293 (100), 281 (36), 239 (67), 183 (56); HRMS (EI): Calcd for $C_{21}H_{26}N_2O$: 322.2045; found: 322.2043.

***N*-Allyl-5-methoxy-4′-methyl-2-(methylamino)diphenylamine (4d)**. Yellow oil (247 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H), 2.77 (s, 3H), 3.70 (s, 3H), 3.85 (br s, 1H), 4.12-4.16 (m, 2H), 5.14-5.18 (m, 1H), 5.21-5.26 (m, 1H), 5.91-6.03 (m, 1H), 6.51-6.57 (m, 2H), 6.66 (d, *J* 8.0 Hz, 1H), 6.68 (d, *J* 2.0 Hz, 1H), 6.78-6.82 (dd, *J* 8.0, 2.0 Hz, 1H), 6.94-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 31.4, 54.1, 56.0, 111.7, 113.1, 114.1, 115.2, 116.9, 127.0, 129.7, 133.6, 134.8, 141.3, 145.8, 151.9. MS (EI): *m/z* (%) 282 [M^+] (61), 253 (100), 226 (63), 224 (22), 211 (44); HRMS (EI): Calcd for $C_{18}H_{22}N_2O$: 282.1732; found: 282.1730.

***N*-Allyl-2-butylamino-5-methoxy-4′-methyldiphenylamine (4e)**. Yellow oil (50 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* 8.0 Hz, 3H), 1.25-1.36 (m, 2H), 1.44-1.54 (m, 2H), 2.23 (s, 3H), 3.02-3.08 (m, 2H), 3.69 (m, 3H), 3.82 (br, 1H), 4.11-4.15 (m, 2H), 5.14-5.18 (m, 1H), 5.22-5.27 (m, 1H), 5.92-6.02 (m, 1H), 6.54-6.59 (m, 2H), 6.65-6.68 (m, 2H), 6.75-6.79 (m, 1H), 6.94-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.4, 31.8, 44.3, 54.1, 56.0, 112.2, 113.1, 114.5, 115.1, 116.9, 127.1, 129.6, 133.9, 134.9, 135.6, 140.4, 145.9, 151.7. MS (EI): *m/z* (%) 324 [M^+] (60), 296 (37), 295 (100), 283 (58), 239 (60), 211 (24); HRMS (EI): Calcd for $C_{21}H_{28}N_2O$: 324.2202; found: 324.2208.

***N*-Allyl-2-benzylamino-5-methoxy-4′-methyldiphenylamine (4f)**. Yellow oil (218 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.65-3.70 (m, 2H), 3.98-4.02 (m, 1H), 4.14-4.18 (m, 2H), 4.26-4.30 (m, 2H), 4.32-4.41 (br, 1H), 5.12-5.17 (m, 1H), 5.20-5.27 (m, 1H), 5.92-6.02 (m, 1H), 6.55-6.63 (m, 3H), 6.68-6.73 (m, 1H), 6.95-7.02 (m, 2H), 7.17-7.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 48.6, 54.1, 56.0, 112.6, 113.0, 114.6, 115.1, 117.1, 127.1, 127.3, 128.6, 129.3, 129.7, 134.0, 134.8, 139.8, 139.9, 145.9, 152.0. MS (EI): *m/z* (%) 358 [M^+] (100), 329 (98), 317 (73), 267 (41), 239 (39), 211 (48); HRMS (EI): Calcd for $C_{24}H_{26}N_2O$: 358.2045; found: 358.2032.

***N*-Allyl-2-allylamino-5-methoxy-4′-methyldiphenylamine (4g)**. Yellow oil (213 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.69-3.76 (m, 5H), 4.05 (br s, 1H), 4.11-4.19 (m, 2H), 5.04-5.10 (m, 1H), 5.11-5.20 (m, 2H), 5.21-5.29 (m, 1H), 5.80-5.90 (m, 1H), 5.93-6.03 (m, 1H),

6.53-6.60 (m, 2H), 6.63-6.70 (m, 2H), 6.72-6.80 (m, 1H), 6.93-7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 47.0, 54.1, 56.0, 112.6, 113.1, 114.4, 115.1, 115.8, 117.0, 127.2, 129.7, 134.0, 134.9, 135.9, 139.8, 145.9, 152.0. MS (EI): *m/z* (%) 308 [M^+] (100), 279 (86), 267 (40), 252 (29), 225 (31); HRMS (EI): Calcd for $C_{20}H_{24}N_2O$: 308.1889; found: 308.1888.

***N*-Butyl-5-methoxy-4′-methyl-2-(methylamino)diphenylamine (4h)**. Yellow oil (241 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* 8.0 Hz, 3H), 1.25-1.36 (m, 2H), 1.59-1.67 (m, 2H), 2.23 (s, 3H), 2.76 (s, 3H), 3.47-3.51 (m, 2H), 3.72 (s, 3H), 3.84 (br s, 1H), 6.48-6.53 (m, 2H), 6.64-6.68 (m, 2H), 6.78-6.83 (m, 1H), 6.95-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.4, 20.5, 29.8, 31.4, 51.1, 56.0, 111.7, 113.1, 113.6, 115.4, 126.6, 129.8, 133.4, 141.7, 146.1, 151.9. MS (EI): *m/z* (%) 298 [M^+] (100), 255 (38), 241 (29), 226 (29), 211 (17); HRMS (EI): *m/z* Calcd for $C_{19}H_{26}N_2O$: 298.2045; found: 298.2050.

***N*-Butyl-2-allylamino-5-methoxy-4′-methyldiphenylamine (4i)**. Yellow oil (230 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, *J* 8.0 Hz, 3H), 1.29-1.39 (m, 2H), 1.59-1.68 (m, 2H), 2.23 (s, 3H), 3.47-3.51 (m, 2H), 3.66-3.73 (m, 5H), 4.04 (br s, 1H), 5.05-5.09 (m, 1H), 5.13-5.19 (m, 1H), 5.79-5.89 (m, 1H), 6.50-6.54 (m, 2H), 6.64-6.67 (m, 2H), 6.74-6.78 (m, 1H), 6.95-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.4, 20.5, 29.8, 47.0, 51.2, 55.9, 112.6, 113.0, 113.9, 115.3, 115.8, 126.7, 129.8, 133.7, 136.0, 140.2, 146.2, 152.0. MS (EI): *m/z* (%) 324 [M^+] (100), 283 (50), 267 (14), 239 (78), 211 (20); HRMS (EI): *m/z* Calcd for $C_{21}H_{28}N_2O$: 324.2202; found: 324.2204.

2-Allylamino-3,4′-dichloro-5-methoxydiphenylamine (4j). Yellow oil (262 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (br s, 1H), 3.46-3.48 (m, 2H), 3.71 (s, 3H), 5.11-5.14 (m, 1H), 5.23-5.28 (m, 1H), 5.92-6.02 (m, 1H), 6.44-6.45 (m, 1H), 6.58 (br s, 1H), 6.66-6.68 (m, 1H), 7.03-7.08 (m, 2H), 7.23-7.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.1, 55.7, 99.9, 105.2, 116.4, 120.6, 126.8, 127.1, 129.5, 130.4, 136.3, 140.5, 140.9, 156.8. MS (EI): *m/z* (%) 324 (25), 322 [M^+] (33), 293 (30), 281 (38), 246 (100), 203 (23); HRMS (EI): Calcd for $C_{16}H_{16}{}^{35}Cl_2N_2O$: 322.0640; found: 322.0638.

2-Allylamino-4′-chloro-5-methoxydiphenylamine (4k). Yellow oil (225 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70-3.76 (m, 5H), 5.11-5.15 (m, 1H), 5.20-5.25 (m, 1H), 5.28 (br s, 1H), 5.88-5.60 (m, 1H), 6.62-6.65 (m, 1H), 6.68 (br s, 1H), 6.70-6.75 (m, 3H), 7.14-7.17 (m, 2H), NH proton not found. Additional ^{1}H spectrum was obtained in DMSO-d_6 revealing both NH protons. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.62 (s, 3H), 3.65-3.70 (m, 2H), 4.48-4.53 (m, 1 H,-NHAll), 5.06-5.10 (m, 1H), 5.15-5.20 (m, 1H), 5.83-5.92 (m, 1H), 6.55-6.60 (m, 2H), 6.62-6.64 (m, 1H), 6.71-6.74 (m, 2H), 7.14-7.17 (m, 2H), 7.37 (br s, 1 H, -NHAr); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.5, 55.9, 109.4, 110.1, 113.8, 116.2, 117.4, 124.6, 129.3, 130.4, 135.8, 136.5, 143.6, 152.8. MS (EI): *m/z* (%) 290 (24), 288 [M^+] (48), 259 (29), 247 (30), 212 (100), 169 (27); HRMS (EI): Calcd for $C_{16}H_{17}{}^{35}ClN_2O$: 288.1029; found: 288.1028.

2-Allylamino-5-chloro-4′-fluorodiphenylamine (4l). Fine colorless crystals (198 mg, 72%), mp: 35-38 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72-3.79 (m, 3H), 5.14-5.26 (m, 3H), 5.88-5.98 (m, 1H), 6.62-6.67 (m, 1H), 6.73-6.78 (m, 3H), 6.84-6.87 (m, 1H), 7.16-7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.2, 109.5 (d, J_{CF} 24 Hz), 111.1 (d, J_{CF} 22 Hz), 113.0 (d, J_{CF} 9 Hz), 116.5,

117.7, 125.2, 129.4, 130.3 (d, J_{CF} 9 Hz), 135.4, 138.6, 143.0, 156.1 (d, J_{CF} 236 Hz); MS (EI): *m/z* (%) 278 (18), 276 [M^+] (37), 247 (46), 235 (20), 200 (100); HRMS (EI): Calcd for $C_{15}H_{14}{}^{35}ClFN$: 276.0830, found: 276.0830.

2-Allylamino-5-chloro-4′-ethoxy-3-methoxydiphenylamine (4m). Yellow oil (232 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (t, *J* 8.0 Hz, 3H), 3.49-3.51 (m, 2H), 3.81 (s, 3H), 3.99-4.06 (m, 2H), 5.08-5.11 (m, 1H), 5.21-5.26 (m, 1H), 5.91-6.00 (m, 1H), 6.19 (br s, 1H), 6.36-6.38 (m, 1H), 6.63-6.65 (m, 1H), 6.86-6.90 (m, 2H), 7.03-7.08 (m, 2H), NH proton invisible; ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 50.5, 56.0, 64.0, 102.6, 106.8, 115.6, 115.8, 123.0, 123.2, 129.3, 135.1, 137.0, 141.6, 154.0, 155.1; MS (EI): *m/z* (%) 334 (22), 332 [M^+] (46), 317 (21), 303 (100), 301 (82), 273 (51); HRMS (EI): Calcd for $C_{18}H_{21}{}^{35}ClN_2O_2$: 332.1292; found: 332.1297.

2-Allylamino-4′,5-dichlorodiphenylamine (4n). Yellow oil (206 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74-3.77 (m, 2H), 4.14 (br s, 1H), 5.07 (br s, 1H), 5.13-5.17 (m, 1H), 5.18-5.24 (m, 1H), 5.84-5.94 (m, 1H), 6.60-6.68 (m, 3H), 7.02-7.06 (m, 2H), 7.14-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.4, 112.6, 116.5, 117.1, 122.0, 124.1, 124.9, 125.9, 129.3, 129.4, 135.0, 142.1, 143.5. MS (EI): *m/z* (%) 294 (27), 292 [M^+] (37), 263 (48), 216 (100), 215 (40); HRMS (EI): Calcd for $C_{15}H_{14}{}^{35}Cl_2N_2$: 292.0534; found: 292.0525.

2-Allylamino-5-methoxy-4′-methyldiphenylamine (4o). Yellow oil (94 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.60-3.80 (m, 5H), 510-5.16 (m, 1H), 5.20-5.28 (m, 1H), 5.30-5.45 (m, 1H), 5.90-6.00 (m, 1H), 6.50-6.60 (m, 1H), 6.67-6.88 (m, 4H), 7.00-7.10 (m, 2H), NH proton invisible; ^{13}C NMR (100 MHz, $CDCl_3$): δ =20.7, 47.9, 55.8, 107.8, 108.6, 114.3, 116.5, 117.2, 117.7, 129.8, 130.0, 132.6, 135.0, 135.8, 142.0. MS (EI: *m/z* (%) 268 [M^+] (51), 239 (32), 227 (32), 212 (100); HRMS (EI): Calcd for $C_{17}H_{20}N_2O$: 268.1576; found: 268.1571.

***N*-Allyl-2-allylamino-4′-chloro-5-methoxydiphenylamine (4p)**. Yellow oil (225 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70-3.74 (m, 5H), 3.93 (br s, 1H), 4.12-4.16 (m, 2H), 5.07-5.10 (m, 1H), 5.13-5.20 (m, 2H), 5.21-5.29 (m, 1H), 5.80-5.90 (m, 1H), 5.91-6.00 (m, 1H), 6.53-6.57 (m, 2H), 6.65-6.68 (m, 2H), 6.77-6.80 (m, 1H), 7.07-7.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.8, 54.1, 56.0, 112.8, 113.6, 115.1, 115.3, 116.0, 117.4, 122.8, 129.0, 133.1, 134.1, 135.7, 139.5, 146.6, 152.0. MS (EI: *m/z* (%) 330 (50), 329 (34), 328 [M^+] (100), 299 (90), 287 (45), 259 (70), 211 (60); HRMS (EI): Calcd for $C_{19}H_{21}{}^{35}ClN_2O$: 328.1342; found: 328.1335.

***N*-Allyl-2-allylamino-4′-ethoxy-5-methoxydiphenylamine (4q)**. Yellow oil (217 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, *J* 8.0 Hz, 3H), 3.69-3.73 (m, 5H), 3.92-4.00 (m, 2H), 4.10-4.15 (m, 3H), 5.06-5.10 (m, 1H), 5.14-5.18 (m, 2H), 5.22-5.28 (m, 1H), 5.81-5.90 (m, 1H), 5.92-6.01 (m, 1H), 6.60-6.38 (m, 4H), 6.72-6.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 47.0, 54.6, 56.0, 64.1, 112.5, 112.6, 114.7, 115.5, 115.8, 116.1, 117.0, 134.8, 135.1, 135.9, 139.7, 142.4, 151.9, 152.0. MS (EI): *m/z* (%) 338 [M^+] (100), 309 (91), 269 (63), 227 (26), 211 (24); HRMS (EI): Calcd for $C_{21}H_{26}N_2O_2$: 338.1994; found: 338.1990.

***N*-Allyl-2-allylamino-3,4′-dichloro-5-methoxydiphenylamine (4r)**. Yellow oil (315 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.58-3.62 (m, 2H), 3.69 (s, 3H), 3.75-3.78 (m, 1H), 4.18-4.22 (m, 2H), 5.00-5.04 (m, 1H), 5.07-5.12 (m, 1H), 5.17-5.27 (m, 2H), 5.75-5.84 (m, 1H), 5.85-5.96 (m, 1H), 6.59-6.65 (m, 3H), 6.83-6.86 (m, 1H), 7.08-7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

49.9, 52.9, 55.9, 113.8, 114.6, 115.9, 116.3, 117.5, 123.2, 126.7, 129.0, 133.7, 136.4, 136.6, 138.5, 146.5, 154.1. MS (EI): *m/z* (%) 366 (13), 364 (72), 362 [M^+] (100), 335 (64), 333 (90), 293 (98), 245 (30); HRMS (EI): Calcd for $C_{19}H_{20}{}^{35}Cl_2N_2O$: 366.0457; found: 366.0441.

***N*-Allyl-2-(allylamino)diphenylamine (4s)**. Yellow oil (216 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73-3.80 (m, 2H), 4.15-4.19 (m, 2H), 4.37 (br s, 1H), 5.07-5.11 (m, 1H), 5.14-5.17 (m, 1H), 5.18-5.20 (m, 1H), 5.22-5.28 (m, 1H), 5.80-5.90 (m, 1H), 5.94-6.03 (m, 1H), 6.60-6.65 (m, 2H), 6.67-6.75 (m, 3H), 7.02-7.07 (m, 1H), 7.12-7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 46.0, 54.0, 111.5, 114.0, 116.2, 117.1, 117.4, 117.7, 127.8, 129.1, 129.3, 132.7, 134.6, 135.4, 145.4, 148.3. MS (EI): *m/z* (%) 264 [M^+] (78), 236 (30), 235 (100), 223 (50), 195 (69); HRMS (EI): Calcd for $C_{18}H_{20}N_2$: 264.1626; found: 264.1625.

***N*-Allyl-2-allylamino-5-fluoro-4′-methyldiphenylamine (4t)**. Yellow oil (220 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.69-3.75 (m, 2H), 4.09-4.15 (m, 2H), 4.22 (br s, 1H), 5.07-5.11 (m, 1H), 5.13-5.16 (m, 1H), 5.17-5.19 (m, 1H), 5.20-5.27 (m, 1H), 5.79-5.88 (m, 1H), 5.91-6.01 (m, 1H), 6.55-6.59 (m, 2H), 6.60-6.63 (m, 1H), 6.78-6.82 (m, 1H), 6.83-6.88 (m, 1H), 6.96-7.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =20.4, 46.6, 54.0, 111.8 (d, J_{CF} 2 Hz), 113.7 (d, J_{CF} 22 Hz), 114.8, 115.7 (d, J_{CF} 27 Hz), 116.0, 117.3, 127.8, 129.8, 133.7, 134.5, 135.4, 141.9, 145.6, 155.2 (d, J_{CF} 235 Hz). MS (EI): *m/z* (%) 296 [M^+] (85), 267 (100), 255 (46), 240 (33), 213 (29); HRMS (EI): Calcd for $C_{19}H_{21}FN_2$: 296.1689; found: 296.1681.

2-Allylamino-*N*-butyl-4′-chloro-5-fluorodiphenylamine (4u). Yellow oil (242 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J 8.0 Hz, 3H), 1.25-1.40 (m, 2H), 1.57-1.67 (m, 2H), 3.45-3.50 (m, 2H), 3.70-3.75 (m, 2H), 4.08 (br s, 1H), 5.10-5.19 (m, 2H), 5.77-5.88 (m, 1H), 6.48-6.54 (m, 2H), 6.60-6.65 (m, 1H), 6.75-6.79 (m, 1H), 6.87-6.93 (m, 1H), 7.08-7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.5, 29.6, 46.5, 51.2, 112.1 (d, J_{CF} 7 Hz), 114.4 (d, J_{CF} 21 Hz), 115.0, 115.8, 116.1 (d, J_{CF} 8 Hz), 122.8, 129.1, 132.3 (d, J_{CF} 8 Hz), 135.3, 142.0 (d, J_{CF} 2 Hz), 146.6, 155.3 (d, J_{CF} 236 Hz). MS (EI): *m/z* (%) 334 (37), 332 [M^+] (77), 289 (36), 275 (14), 249 (53), 247 (100); HRMS (EI): Calcd for $C_{19}H_{22}{}^{35}ClFN_2$: 332.1456; found: 332.1463.

***N*-Allyl-2-allylamino-5-chloro-4′-methyldiphenylamine (4v)**. Yellow oil (150 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.71-3.76 (m, 2H), 4.08-4.14 (m, 2H), 4.41 (br s, 1H), 5.08-5.26 (m, 4H), 5.78-5.87 (m, 1H), 5.90-6.00 (m, 1H), 6.55-6.62 (m, 3H), 6.96-7.00 (m, 2H), 7.02-7.05 (m, 1H), 7.07-7.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 46.1, 54.1, 112.3, 114.8, 116.1, 117.4, 121.3, 127.4, 127.8, 128.8, 129.8, 134.1, 134.5, 135.0, 144.0, 145.6. MS (EI): *m/z* (%) 314 (43), 312 [M^+] (96), 285 (45), 283 (100), 271 (56), 229 (36); HRMS (EI): Calcd for $C_{19}H_{21}{}^{35}ClN_2$: 312.1391; found: 312.1391.

2-Allylamino-3,4′,5-trichlorodiphenylamine (4w). Yellow oil (277 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.42 (br s, 1H), 3.51-3.57 (m, 2H), 5.13-5.16 (m, 1H), 5.24-5.30 (m, 1H), 5.90-6.00 (m, 1H), 6.31-6.35 (m, 1H), 6.88-6.90 (m, 1H), 7.01-7.04 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.2, 113.3, 116.7, 120.2, 120.9, 127.4, 129.4, 129.5, 129.7, 132.6, 136.0, 140.0, 140.3. MS (EI): *m/z* (%) 328 (23), 326 [M^+] (23), 299 (46), 285 (18), 250 (100), 179 (14); HRMS (EI): Calcd for $C_{15}H_{13}{}^{35}Cl_3N_2$: 326.0118; found: 326.0130.

***N*-Allyl-2-allylamino-3,4′,5-trichlorodiphenylamine (4x)**. Yellow oil (93 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66-3.70 (m, 2H), 4.13-4.17 (m, 3H), 5.04-5.10 (m, 2H), 5.12-5.27 (m, 2H), 5.73-5.83 (m, 1H), 5.85-5.93 (m, 1H), 6.60-6.65 (m, 2H), 6.98-7.00 (m, 1H), 7.11-7.15 (m, 2H), 7.22-7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.8, 52.6, 116.1, 116.6, 118.0, 123.8, 124.7, 125.4, 127.7, 128.8, 129.1, 133.2, 135.8, 137.2, 141.5, 146.1. MS (EI): *m/z* (%) 368 (69), 367 (19), 366 [M^+] (70), 339 (99), 337 (100), 310 (55), 249 (38); HRMS (EI): Calcd for $C_{18}H_{17}{}^{35}Cl_3N_2$: 366.0457; found: 366.0441.

2-Allylamino-5-methoxy-4′-methyl-*N*-(prop-2-ynyl)diphenylamine (4y). Yellow oil (236 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22-2.26 (m, 4H), 3.69 (s, 3H), 3.72-3.75 (m, 2H), 4.16 (br s, 1H), 4.22-4.25 (m, 2H), 5.06-5.10 (m, 1H), 5.16-5.21 (m, 1H), 5.82-5.92 (m, 1H), 6.65-6.70 (m, 3H), 6.77-6.79 (m, 1H), 6.82-6.84 (m, 1H), 7.00-7.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 40.5, 46.9, 56.0, 72.5, 80.4, 112.5, 113.7, 114.5, 114.9, 115.9, 128.1, 129.7, 133.6, 135.8, 139.6, 144.9, 152.0. MS (EI): *m/z* (%) 306 [M^+] (60), 265 (100), 239 (29), 211 (25), 160 (20); HRMS (EI): Calcd for $C_{20}H_{22}N_2O$: 306.1732; found: 306.1732.

2-Allylamino-5-methoxy-4′-methyl-*N*-(pent-4-enyl)diphenylamine (4z). Yellow oil (255 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.79 (m, 2H), 2.06-2.11 (m, 2H), 2.23 (s, 3H), 3.50-3.55 (m, 2H), 3.68-3.72 (s, 5H), 4.03 (br s, 1H), 4.94-4.99 (m, 2H), 5.02-5.09 (m, 1H), 5.13-5.18 (m, 1H), 5.75-5.88 (m, 2H), 6.51-6.54 (m, 2H), 6.65-6,68 (m, 2H), 6.75-6.79 (m, 1H), 6.96-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 26.8, 31.4, 47.0, 50.9, 56.0, 112.6, 113.0, 114.0, 115.2, 115.3, 115.8, 126.9, 129.8, 133.5, 135.9, 138.1, 140.1, 146.1, 152.0. MS (EI): *m/z* (%) 336 (100), 295 (31), 281 (17), 252 (20), 239 (91), 224 (18), 211 (20); HRMS (EI): Calcd for $C_{22}H_{28}N_2O$: 336.2202; found: 336.2200.

2-Allylamino-5-methoxy-4′-methyl-*N*-(hex-5-enyl)diphenylamine (4za). Yellow oil (277 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38-146 (m, 2H), 1.64-1.72 (m, 2H), 2.03-2.10 (m, 2H), 2.23 (s, 3H), 3.48-.3.53 (m, 2H), 3.68-3.73 (m, 5H), 4.03 (br s, 1H), 4.95-5.01 (m, 2H), 5.05-5.10 (m, 1H), 5.13-5.19 (m, 1H), 5.73-5.90 (m, 2H), 6.50-6.55 (m, 2H), 6.65-6.68 (m, 2H), 6.75-6.79 (m, 1H), 6.95-6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 26.6, 27.2, 33.7, 47.0, 51.3, 56.0, 112.6, 113.0, 113.9, 114.8, 115.3, 115.8, 126.8, 129.8, 133.6, 136.0, 138.7, 140.1, 146.2, 152.0. MS (EI): *m/z* (%) 350 (100), 309 (26), 281 (18), 267 (17), 240 (47), 239 (69), 211 (19), 160 (20); HRMS (EI): Calcd for $C_{23}H_{30}N_2O$: 350.2358; found: 350.2356.

General procedure for *N*-protection of 4 with ethyl chloroformate

Ethyl chloroformate (2 mmol) and dry pyridine (1.3 mmol) were carefully added to a cooled (~0 °C) solution of **4** (1 mmol) in toluene (5 mL). The mixture was heated at 80 °C until the reaction was complete (0.5 – 1 h, TLC monitoring), and then cooled and acidified to pH 2 with 2 N HCl. The organic phase was separated, washed with water, and dried (Na_2SO_4). After solvent evaporation the crude product was subjected to column chromatography (hexane/ethyl acetate, 4:1).

Ethyl allyl-{2-[*N*-allyl-*N*-(4-methylphenyl)amino]-4-methoxyphenyl}carbamate (5a). Yellow oil (334 mg, 88%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.08 (t, *J* 7.1 Hz, 3H), 2.19 (s, 3H), 3.04-3.08 (m, 2H), 3.73 (s, 3H), 3.91-3.97 (m, 2H), 4.14-4.18 (m, 2H), 4.98-5.04 (m, 2H), 5.12-

5.16 (m, 1H), 5.19-5.24 (m, 1H), 5.73-5.82 (m, 1H), 5.86-5.94 (m, 1H), 6.61-6.65 (m, 2H), 6.69-6.71 (m, 1H), 6.73-6.77 (m, 1H), 6.94-6.97 (m, 2H), 7.08-7.10 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 14.8, 20.4, 51.8, 54.5, 55.8, 61.2, 111.1, 113.4, 117.0, 117.1, 117.2, 128.1, 129.5, 130.8, 132.4, 134.6, 135.4, 145.6, 145.8, 155.1, 159.3. MS (EI): *m/z* (%) 380 [M^+] (89), 351 (69), 311 (46), 278 (55), 238 (100), 224 (33); HRMS (EI): Calcd for $C_{23}H_{28}N_2O_3$: 380.2100; found: 380.2097.

Ethyl allyl-{2-[allyl-(4-ethoxyphenyl)amino]-4-methoxyphenyl}carbamate (5b). Yellow oil (340 mg, 83%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.06 (t, *J* 7.1 Hz, 3H), 1.27 (t, *J* 6.9 Hz, 3H), 3.71 (s, 3H), 3.87-3.96 (m, 5H), 4.13-4.17 (m, 3H), 4.97-5.02 (m, 2H), 5.09-5.13 (m, 1H), 5.17-5.22 (m, 1H), 5.71-5.80 (m, 1H), 5.83-5.92 (m, 1H), 6.65-6.74 (m, 6H), 7.00-7.03 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 13.9, 14.2, 50.7, 54.3, 54.9, 60.2, 63.0, 109.0, 111.3, 114.6, 116.2, 116.3, 119.1, 129.0, 131.4, 133.8, 134.8, 140.9, 145.3, 152.5, 154.1, 158.3. MS (EI): *m/z* (%) 410 [M^+] (100), 381 (46), 368 (29), 308 (32), 281 (33), 255 (16); HRMS (EI): Calcd for $C_{24}H_{30}N_2O_4$: 410.2206; found: 410.2189.

Ethyl allyl-{2-[allyl-(4-chlorophenyl)amino]-6-chloro-4-methoxyphenyl}carbamate (5c). Yellow oil (356 mg, 82%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.06 (t, *J* 6.8 Hz, 3H), 3.62-3.68 (m, 1H), 3.75 (s, 3H), 3.82-3.85 (m, 1H), 3.93-4.00 (m, 1H), 4.06-4.13 (m, 1H), 4.23-4.29 (m, 1H), 4.94-4.99 (m, 2H), 5.14-5.24 (m, 2H), 5.71-5.80 (m, 1H), 5.84-5.92 (m, 1H), 6.70-6.74 (m, 3H), 6.96-6.99 (m, 1H), 7.13-7.17 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 13.8, 51.2, 53.8, 55.4, 60.6, 112.0, 112.5, 116.9, 117.3, 117.9, 122.8, 127.9, 132.9, 133.2, 133.6, 135.3, 145.6, 146.0 153.7, 158.6. MS (EI): *m/z* (%) 436 (18), 434 [M^+] (23), 405 (41), 392 (58), 305 (53), 293 (100), 269 (11); HRMS (EI): Calcd for $C_{22}H_{24}{}^{35}Cl_2N_2O_3$: 434.1164; found: 434.1147.

Ethyl allyl-{2-[allyl(phenyl)amino]phenyl}carbamate (5d). Yellow oil (316 mg, 94%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.06 (t, *J* 7.1 Hz, 3H), 3.93-3.98 (m, 4H), 4.16-4.19 (m, 2H), 4.97-5.03 (m, 2H), 5.12-5.15 (m, 1H), 5.18-5.24 (m, 1H), 5.74-5.82 (m, 1H), 5.86-5.94 (m, 1H), 6.64-6.67 (m, 2H), 6.69-6.73 (m, 1H), 7.09-7.13 (m, 2H), 7.19-7.23 (m, 3H), 7.27-7.32 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80°C): δ 13.8, 50.8, 53.2, 60.4, 115.3, 116.3, 116.5, 117.9, 125.1, 127.8, 128.0, 128.1, 130.9, 133.6, 134.2, 137.6, 143.6, 147.0, 154.0. MS (EI): *m/z* (%) 336 [M^+] (45), 307 (70), 294 (62), 267 (29), 221 (48), 195 (100); HRMS (EI): Calcd for $C_{21}H_{24}N_2O_2$: 336.1838; found: 336.1832.

Ethyl allyl-{2-[allyl-(4-methylphenyl)amino]-4-fluorophenyl}carbamate (5e). Yellow oil (331 mg, 95%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.06 (t, *J* 7.0 Hz, 3H), 2.19 (s, 3H), 3.57-3.83 (m, 2H), 3.88-3.94 (m, 2H), 4.16-4.23 (m, 2H), 4.97-5.04 (m, 2H), 5.11-5.14 (m, 1H), 5.17-5.22 (m, 1H), 5.71-5.79 (m, 1H), 5.83-5.92 (m, 1H), 6.66-6.69 (m, 2H), 6.89-6.98 (m, 4H), 7.13-7.18 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 13.8, 19.6, 50.5, 53.9, 60.4, 110.5 (d, J_{CF} 22 Hz), 112.5 (d, J_{CF} 22 Hz), 116.5, 117.7, 128.6, 128.7, 128.8, 132.3 (d, J_{CF} 10 Hz), 132.5 (d, J_{CF} 3 Hz), 133.5, 134.2, 144.3, 145.6 (d, J_{CF} 10 Hz), 153.8, 160.6 (d, J_{CF} 244 Hz). MS (EI): *m/z* (%) 368 [M^+] (65), 326 (68), 281 (32), 266 (42), 239 (40), 227 (100); HRMS (EI): Calcd for $C_{22}H_{25}FN_2O_2$: 368.1900; found: 368.1913.

Ethyl 2-methylpropenyl-{2-[allyl-(4-methylphenyl)amino]-4-methoxyphenyl}carbamate (5f). Yellow oil (327 mg, 83%). ^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C): δ 1.07 (t, J 7.0 Hz, 3H), 1.63 (s, 3H), 2.18 (s, 3H), 3.05 (s, 2H), 3.71 (s, 3H), 3.90-3.95 (m, 2H), 4.13-4.20 (m, 2H), 4.66 (s, 1H), 4.73 (s, 1H), 5.12-5.15 (m, 1H), 5.18-5.23 (m, 1H), 5.86-5.93 (m, 1H), 6.61-6.64 (m, 2H), 6.69 (d, *J* 2.9 Hz, 1H), 6.72-6.75 (dd, *J* 8.7, 2.9 Hz, 1H), 6.93-6.96 (m, 2H), 7.09 (d, *J* 8.7 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C): δ 13.9, 19.5, 19.6, 53.6, 54.9, 60.3, 110.1, 111.9, 112.5, 116.3, 127.2, 128.4, 128.6, 129.7, 131.5, 134.3, 134.5, 141.0, 144.6, 147.6, 154.4, 158.3. MS (EI): *m/z* (%) 394 (64) [M^+], 365 (46), 352 (92), 321 (17), 292 (43), 239 (100); HRMS (EI): Calcd for $C_{24}H_{30}N_2O_3$: 394.2256; found: 394.2258.

Ethyl allyl-{2-[penten-4-yl-(4-methylphenyl)amino]-4-methoxyphenyl}carbamate (5g). Colorless oil (396 mg, 97%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 ^{o}C): δ 1.06 (t, *J* 7.0 Hz, 3H), 1.63-1.69 (m, 2H), 2.01-2.07 (m, 2H), 2.18 (s, 3H), 3.45-3.50 (m, 2H), 3.71 (s, 3H), 3.80-4.25 (m, 4H), 4.92-5.01 (m, 4H), 5.70-5.84 (m, 2H), 6.58-6.62 (m, 2H), 6.65 (d, *J* 2.8 Hz, 1H), 6.71-6.74 (dd, *J* 8.7, 2.8 Hz, 1H), 6.93-6.96 (m, 2H), 7.06 (d, *J* 8.7 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 ^{o}C): δ 13.9, 19.5, 25.9, 30.2, 50.6, 50.7, 54.9, 60.3, 109.9, 112.4, 114.4, 116.3, 116.4, 127.2, 128.7, 129.9, 131.7, 133.7, 137.5, 144.8, 144.9, 154.2, 158.4. MS (EI): *m/z* (%) 408 (84), 353 (27), 313 (33), 312 (100), 283 (12), 239 (67), 224 (20); HRMS (EI): Calcd for $C_{25}H_{32}N_2O_3$: 408.2413; found: 408.2414.

General procedure for the ring closing metathesis of 5. The protected diamine 5 (0.25 mmol) was dissolved in CH_2Cl_2 (25 mL), after which the Grubbs catalyst (5 mol%, 0.0125mmol) was added and the reaction mixture was stirred at 45 °C under argon atmosphere for the time specified in Table 2. The solvent was removed under vacuum and column chromatography (hexane /EtOAc, 9:1 to 4:1) of the crude product was performed to afford 6, generally as a yellow oil.

Ethyl 8-methoxy-6-(4-methylphenyl)-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6a). Yellow oil (71 mg, 81%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.12 (t, *J* 7.0 Hz, 3H), 2.18 (m, 3H), 3.65 (s, 3H), 4.01-4.06 (m, 4H), 4.16-4.18 (m, 2H), 5.70-5.75 (m, 1H), 5.82-5.89 (m, 1H), 6.46-6.48 (m, 1H), 6.61-6.64 (m, 1H), 6.81-6.84 (m, 2H), 7.00-7.03 (m, 2H), 7.15-7.18 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 14.0, 19.6, 46.2, 47.4, 54.9, 60.5, 108.8, 110.2, 117.6, 117.7, 127.3, 128.4, 129.0, 129.7, 129.8, 142.5, 144.5, 154.4, 157.4, one signal invisible. MS (EI): *m/z* (%) 352 [M^+] (100), 312 (11), 311 (52), 263 (52), 239 (73); HRMS (EI): Calcd for $C_{21}H_{24}N_2O_3$: 352.1787; found: 352.1786.

Ethyl 6-(4-ethoxyphenyl)-8-methoxy-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6b). Yellow oil (92 mg, 96%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.12 (t, *J* 6.8 Hz, 3H), 1.29 (t, *J* 7.0 Hz, 3H), 3.60 (s, 3H), 3.95-4.00 (m, 2H), 4.01-4.06 (m, 2H), 4.11-4.15 (m, 4H), 5.69-5.74 (m, 1H), 5.76-5.82 (m, 1H), 6.27 (d, *J* 2.8 Hz, 1H), 6.49-6.52 (dd, *J* 8.8, 2.8 Hz, 1H), 6.80-6.83 (m, 2H), 6.90-6.93 (m, 2H), 7.07 (d, *J* 8.8. Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 14.0, 14.2, 47.0, 18.3, 54.7, 60.5, 63.0, 107.3, 108.7, 115.1, 121.4, 121.5, 126.7, 129.9, 130.0, 140.9, 143.8, 153.3, 154.6, 157.6. MS (EI): *m/z* (%) 382 [M^+] (100), 355 (22), 341 (81), 297 (42), 269 (80), 253 (23); HRMS (EI): Calcd for $C_{22}H_{26}N_2O_4$: 382.1893; found: 382.1880.

Ethyl 6-(4-chlorophenyl)-8-methoxy-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6c). Yellow oil (85 mg, 84%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 0.95-1.00 (m, 3H), 3.55-3.61 (m, 1H), 3.68 (s, 3H), 3.85-3.90 (m, 1H), 3.91-3.98 (m, 1H), 4.07-4.26 (m, 1H), 4.65-4.70 (m, 1H), 5.78-5.82 (m, 1H), 5.86-5.91 (m, 1H), 6.51-6.54 (m, 1H), 6.89-6.94 (m, 4H), 7.20-7.25 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 13.9, 46.3, 46.8, 55.3, 60.8, 110.5, 119.7, 119.9, 123.9, 126.9, 128.3, 130.7, 130.9, 133.7, 144.9, 146.2, 154.1, 158.2. MS (EI): *m/z* (%) 408 (65), 407 (25), 406 [M^+] (88), 333 (39), 304 (81), 293 (100), 278 (20); HRMS (EI): Calcd for $C_{20}H_{20}{}^{35}Cl_2N_2O_3$: 406.0851, found: 406.0836.

Ethyl 6-phenyl-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6d). Colorless oil (67 mg, 87%). ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.12 (t, *J* 7.0 Hz, 3H), 3.96-3.99 (m, 2H), 4.02-4.07 (m, 2H), 4.19-4.22 (m, 2H), 5.73-5.77 (m, 1H), 5.87-5.92 (m, 1H), 6.75-6.78 (m, 1H), 6.81-6.84 (m, 2H), 7.09-7.18 (m, 5H), 7.31-7.35 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 13.9, 46.0, 46.4, 60.7, 115.5, 118.4, 123.5, 126.0, 126.7, 128.0, 128.3, 128.9, 129.4, 136.7, 140.6, 146.4, 154.0. MS (EI): *m/z* (%) 308 [M^+] (100), 267 (64), 235 (48), 219 (53), 206 (38); HRMS (EI): Calcd for $C_{19}H_{20}N_2O_2$: 308.1525; found: 308.1531.

Ethyl 8-fluoro-6-(4-methylphenyl)-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6e). Fine colorless crystals (77 mg, 98%), mp 83-86 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C): δ 1.14 (t, *J* 7.0 Hz, 3H), 2.24 (s, 3H), 4.05-4.13 (m, 4H), 4.17-4.20 (m, 2H), 5.74-5.78 (m, 1H), 5.81-5.87 (m, 1H), 6.56-6.60 (m, 1H), 6.73-6.78 (m, 1H), 6.89-6.92 (m, 2H), 7.06-7.09 (m, 2H), 7.24-7.28 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6, 80 °C): δ 14.0, 19.6, 46.4, 47.8, 60.8, 108.4 (d, J_{CF} 22 Hz), 110.1 (d, J_{CF} 23 Hz), 119.5, 126.7, 129.3, 130.0, 130.1, 130.3, 130.8 (d, J_{CF} 10 Hz), 143.8 (d, J_{CF} 11 Hz), 144.3, 154.3, 159.9 (d, J_{CF} 241 Hz). MS (EI): *m/z* (%) 340 [M^+] (73), 299 (55), 267 (24), 255 (42), 227 (100); HRMS (EI): Calcd for $C_{20}H_{21}FN_2O_2$: 340.1587; found: 340.1589.

Ethyl 8-methoxy-3-methyl-6-(4-methylphenyl)-5,6-dihydro-1,6-benzodiazocine-1(2*H*)-carboxylate (6f). Yellow oil (82 mg, 90%). ^{1}H NMR (600 MHz, DMSO-d_6, 80 ^{o}C): δ 1.09-1.15 (m, 3H), 1.64 (s, 3H), 2.22 (s, 3H), 3.64 (s, 3H), 3.94-4.07 (m, 4H), 4.09-4.12 (m, 2H), 5.54-5.58 (m, 1H), 6.45 (br s, 1H), 6.58-6.61 (dd, *J* 8.7, 2.7 Hz, 1H), 6.83-6.86 (m, 2H), 7.00-7.03 (m, 2H), 7.15 (d, *J* 8.7 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6, 80 ^{o}C): δ 13.9, 19.6, 22.3, 46.2, 51.9, 54.8, 60.6, 108.5, 109.8, 117.8, 117.9, 121.0, 128.5, 129.0, 129.5, 137.6, 142.8, 144.4, 154.5, 157.3. MS (EI): *m/z* (%) 366 (100), 354 (31), 311 (29), 277 (62), 264 (60), 239 (49), 213 (31), 187 (20); HRMS (EI): Calcd for $C_{22}H_{26}N_2O_3$: 366.1943; found: 366.1931.

Ethyl 10-methoxy-8-(4-methylphenyl)-5,6,7,8-tetrahydro-1,8-benzodiazecine-1(2*H*)-carboxylate (6g). Yellow oil (41 mg, 43%). Data worked out from the inseparable *Z* and *E* isomer mixture: ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.95 (t, *J* 7.0 Hz, 3H), 1.00 (t, *J* 7.0 Hz, 3H), 1.20-1.25 (m, 2H), 1.60-1.66 (m, 3H), 2.14-2.20 (m, 6H), 2.22-2.32 (m, 2H), 3.10-3.50 (m, 4H), 3.60-3.84 (m, 11H), 4.10-4.20 (m, 2H), 4.57-4.70 (m, 2H), 5.10-5.20 (m, 1H), 5.22-5.30 (m, 1H), 5.36-5.44 (m, 1H), 5.49-5.57 (m, 1H), 6.56-6.60 (m, 2H), 6.64-6.79 (m, 6H), 6.86-6.97 (m, 4H), 7.02-7.10 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 13.7, 13.8, 18.9, 19.5, 23.2, 25.3, 28.9, 31.1, 44.0, 52.2, 54.9, 55.0, 59.8, 60.0, 109.4, 110.1, 111.5, 117.9, 123.6, 127.9, 128.1, 128.4,

129.4, 131.1, 133.7, 145.6, 146.6, 154.3, 158.1, 158.8. MS (ESI): *m/z* (%) 381.22 $[M+H]^+$, 403.20 $[M+Na]^+$, 783.41 $[2M+Na]^+$; HRMS (ESI): Calcd for $C_{23}H_{28}N_2O_3Na$: 403.1998, found: 403.1991.

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