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Pd_2dba_3/P(*i*-BuNCH$_2$CH$_2$)$_3$N: a highly efficient catalyst for the one-pot synthesis of *trans*-4-*N*,*N*-diarylaminostilbenes and *N*,*N*-diarylaminostyrenes

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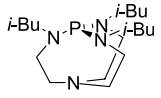
Abstract—A Pd_2dba_3/P(*i*-BuNCH$_2$CH$_2$)$_3$N catalyzed one-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes and both symmetrically and unsymmetrically substituted *N*,*N*-diarylaminostyrene derivatives is reported. The procedure involves two or more palladium catalyzed sequential coupling reactions (an amination and an inter-molecular Heck reaction) in one-pot using the same catalyst system with two different aryl halides, including aryl chlorides and hetero aryl halides as the coupling partners.

1. Introduction

Palladium catalyzed C–C and C-hetero-atom bond forming reactions represent one of the most powerful methods for the synthesis of several complex molecular structures such as gilvocarcines and pradimicines.[1] The scope of these methods has been enhanced by the discovery of new ligands that facilitate coupling reactions more efficiently under mild reaction conditions. In recent years our explorations of the chemistry of commercially available proazaphosphatranes such as **1**, first synthesized in our laboratories,[2] have shown them to be efficient ligands in palladium-catalyzed N-arylation,[3] Suzuki[4] and Stille[5] couplings, including those of neutral as well as electron-rich and electron-deficient aryl chlorides. Moreover, proazaphosphatranes can also function as strong non-ionic stoichiometric bases that facilitate a variety of useful organic transformations.[6] Recently, palladium-catalyzed sequential coupling reactions have emerged as a powerful tool for the synthesis of complex organic molecules from readily available starting materials in a single pot reaction.[7] Among them, the palladium-catalyzed synthesis of *N*-aryl-2-benzylindolines via a sequential N-arylation/cyclization/C-arylation reaction between 2-allylaniline and aryl halides demonstrated the importance of such reactions in modern synthetic chemistry.[8]



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N,*N*-Diarylaminostilbenes are versatile compounds that have found interesting applications in the field of photochemistry as electro photographic photoconductors and photoreceptors.[9] A series of recent reports showed that the fluorescence enhancement of *N*,*N*-diarylaminostilbenes has been achieved by *N*-phenyl substitution[10] and also their use as new ionophores for transition metals.[11] The traditional approaches to the synthesis of these compounds begin from aniline and the corresponding aryl halides via a multi step process.[12] Recently, the synthesis of *trans*-4-*N*,*N*-diarylaminostilbenes from the corresponding halostilbenes or aminostilbenes, using palladium catalyzed amination reactions, has also been reported.[10,11]

Very recently, we disclosed in preliminary form an efficient one-pot procedure for the synthesis of *trans*-4-*N*,*N*-diarylaminostilbenes via a sequential double amination/arylation protocol using Pd_2dba_3/**1** as the catalyst.[13] In this full paper we report the results of our detailed investigation of the one-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes and both symmetrically and unsymmetrically substituted *N*,*N*-diarylaminostyrenes. Furthermore, we report the synthesis of dibenz[*b*,*d*]azepine via a palladium-catalyzed one-pot amination/Suzuki reaction.

Keywords: Proazaphosphatranes; Palladium; Amination; C–C Coupling; *trans*-4-*N*,*N*,-Diarylaminostilbenes; Heck reaction.
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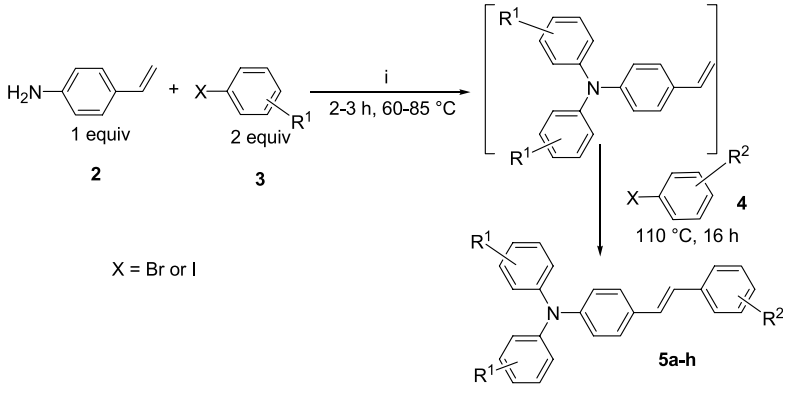
2. Results and discussion

2.1. One-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes (identical aryl groups on the nitrogen)

The optimized reaction conditions for the one-pot synthesis of symmetrically and unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes have previously been reported.[13] From these experiments, it is evident that the title compounds were formed via a double amination, followed by an inter-molecular Heck reaction. Thus, the reaction of **2** with 2 equiv of the first aryl halide **3** completed the double amination as judged by TLC (Scheme 1). The subsequent Heck reaction was initiated by adding 1.2 equiv of the second aryl halide **4** followed by increasing the temperature to 110 °C for an additional 16 h (see Table 1 for details).

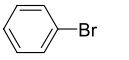
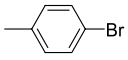
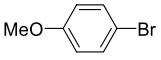
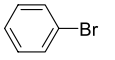
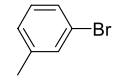
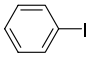
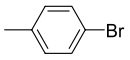
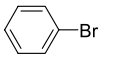
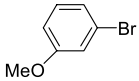
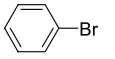
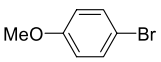
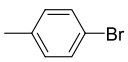
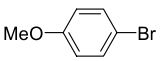
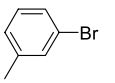
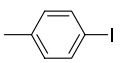
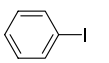
The products in entries 5 and 7 are novel and their structures were confirmed on the basis of their ^{1}H and ^{13}C NMR and their high-resolution mass spectra. The yield for **5a** (86%) is comparable to that reported in a patented procedure (89%) involving the single-step reaction of 4-methyldiethylbenzylphosphonate with 4-*N*,*N*-diphenylaminobenzaldehyde.[14] However, the yield of **5a** is substantially better than that attained in the same patent via the Wittig reaction of 4-methylbenzyltriphenylphosphonium chloride with the aforementioned aldehyde (72%) and also to the overall yield (46%) reported for an earlier three-step synthesis.[14] Although the remaining compounds in entries 2, 3, 4, 6, and 8 were reported earlier,[9,15] no yields were provided. The difference in reactivity of 4-aminostyrene at different temperatures under our reaction conditions allowed us to couple a variety of aryl halides at the nitrogen and the double bond to synthesize unsymmetrically substituted title compounds.



i. $Pd_2(dba)_3$, **1**, NaO-*t*-Bu, dry toluene.

Scheme 1.

Table 1. One-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes

Entry	Aryl halide (**3**)	Time (h)	Temperature *T* (°C)	Aryl halide (**4**)	Yield (%)[a,b]
1		3	60		86 (46)[c]
2		3	60		60[c]
3		2	85		83
4		2	85		91
5		2	85		75
6		3	60		44
7		3	60		43
8		3	60		81

[a] Isolated yield, average of two runs.
[b] Reaction conditions: $Pd_2(dba)_3$ (2 mol%), **1** (4 mol%), NaO-*t*-Bu (3.5 equiv), aryl halide **3** (2 equiv), aryl halide **4** (1.2 equiv), 10 mL of dry toluene, argon atmosphere.
[c] Literature yield.

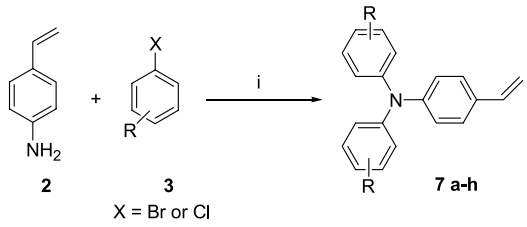
2.2. One-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes (different aryl groups on nitrogen)

Encouraged by the results obtained via Scheme 1, we investigated the reaction of **2** with different aryl halides by changing the mode of coupling, namely, by carrying out mono-amination using the first aryl halide followed by the second amination and inter-molecular Heck reaction, by addition of the second aryl halide and heating at 110 °C for an additional 16 h (Scheme 2). This reaction was also found to be quite general, allowing the synthesis of a variety of the title compounds using the same protocol.

Our yield of 78% for **6a** is lower than that reported in a patent,[9] which involved the reaction of 4-[*N*-(4-methylphenyl)-*N*-phenylamino]benzaldehyde with diethylbenzylphosphonate (91%). It should be noted that the higher literature yield[9] for **6a** was achieved in a single reaction involving two reactants, one of which required prior synthesis. When this requirement is taken into account, the overall literature yield is 50%[16] compared with our one-pot yield of 78%. The compounds in entries 6 and 10 are novel, while the products in entries 4 and 9 were reported previously,[15] although no yield was given. It is also worthy of note that although when the less reactive aryl chlorides were used as the first aryl halide (entries 7, 8, and 9), the yields for the target compounds were still excellent although a higher temperature and longer reaction time was required. It may be noted that while the application of less expensive aryl chlorides further reduces the cost of the total procedure, additional energy costs would be incurred.

2.3. One-pot synthesis of diarylaminostyrenes with identical aryl groups on the nitrogen

As with *N*,*N*-diarylaminostilbenes, *N*,*N*-diarylaminostyrenes have also been used as hole-transport materials for organic electroluminescent devices and electrophotographic photoreceptors.[17] Moreover, this class of compounds serves as a precursor for the synthesis of a variety of photo chemically valuable target molecules such as *N*,*N*-diarylaminostilbenes, which are building blocks for the synthesis of oligo(phenylenevinylene) (OPV) dyes containing diphenylamino substituents.[18] Several methods are available in the literature for the synthesis of *N*,*N*-diarylaminostyrenes possessing identical aryl groups on the nitrogen, but most of these approaches are multi-step procedures.[17b] It is evident from the literature that a simple, mild, and efficient one-pot procedure for the synthesis of these compounds would be very useful. Herein, we report such a protocol using the same catalyst system employed earlier in this paper and the results are collected in Scheme 3 (Table 2).



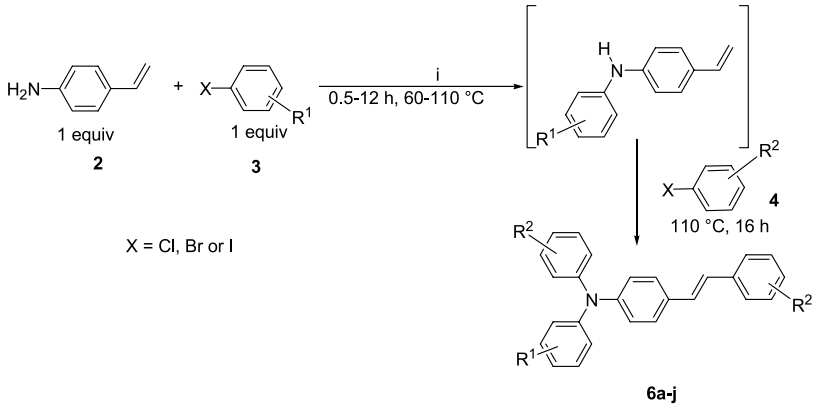
i. $Pd_2(dba)_3$, **1**, NaO-*t*-Bu, dry toluene.

Scheme 3.

The compounds in entries 5 and 6 are novel and the structures of the products were confirmed on the basis of their spectral data. The yields of *N*,*N*-diarylaminostyrenes obtained in entries 1, 2, and 8 using our protocol are better than the two step procedure reported in a patent, which involve a palladium-catalyzed amination to synthesize the corresponding 4-chlorotriphenylamine followed by a Grignard reaction with vinyl chloride.[17b] The products in entries 3 and 7 were reported in patents,[19] but no yields were given. The reaction of less reactive 4-chlorotoluene also afforded **7** in 78% yield, using the same amount of catalyst loading, but an elevated temperature and a longer reaction time was required (Table 3, entry 8).

2.4. One-pot double amination for the synthesis of unsymmetrically substituted *N*,*N*-diarylaminostyrenes

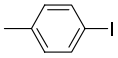
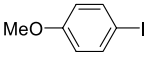
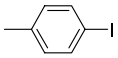
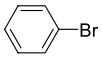
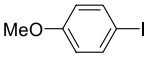
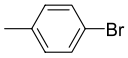
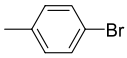
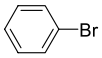
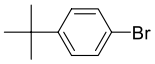
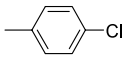
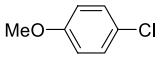
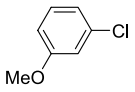
Unlike symmetrically substituted *N*,*N*-diarylaminostyrenes, a general procedure for the synthesis of unsymmetrically substituted *N*,*N*-diarylaminostyrenes is not known in the literature, owing primarily to the difficulty in controlling the mono-amination step in known procedures such as Ullmann coupling followed by a Vilsmeir and Wittig reaction sequence.



i. $Pd_2(dba)_3$, **1**, NaO-*t*-Bu, dry toluene.

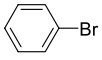
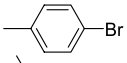
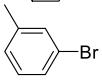
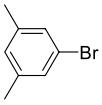
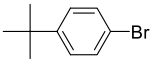
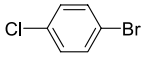
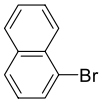
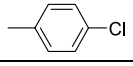
Scheme 2.

Table 2. One-pot synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes

Entry	Aryl halide (**3**)	Time (h)	Temperature *T* (°C)	Aryl halide (**4**)	Yield (%)[a,b]
1		3	60		78 (50)[c]
2		3	60		79
3		3	60		52
4		3	60		81
5		3	85		50
6		3	85		71
7		12	110		44
8		12	110		71
9		12	110		65
10		0.5	110		74

[a] Isolated yield, average of two runs.
[b] Reaction conditions: $Pd_2(dba)_3$ (2 mol%), **1** (4 mol%), NaO-*t*-Bu (3.5 equiv), aryl halide **3** (2 equiv), aryl halide **4** (1.2 equiv), 10 mL of dry toluene, argon atmosphere.
[c] Literature yield.

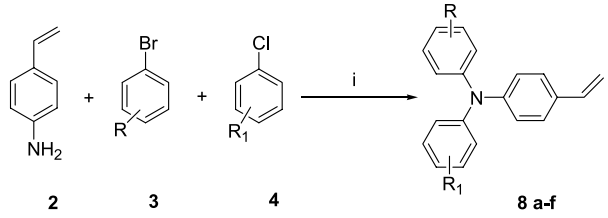
Table 3. One-pot synthesis of symmetrically substituted *N*,*N*-diarylaminostyrenes

Entry	Aryl halide	Time (h)	Temperature *T* (°C)	Yield (%)[a,b]
1		3	60	90 (78)[c]
2		3	85	86 (77)[c]
3		3	85	86[c]
4		3	85	81
5		3	85	91
6		3	85	78
7		12	100	86
8		16	110	78

[a] Isolated yield, average of two runs.
[b] Reaction conditions: $Pd_2(dba)_3$ (2 mol%), **1** (4 mol%), NaO-*t*-Bu (2.5 equiv), aryl halide **3** (2.1 equiv), 10 mL of dry toluene, argon atmosphere.
[c] Literature yield.

We were able to synthesize several derivatives of **8** with two different aryl groups on nitrogen in a one-pot multicomponent reaction using the Pd_2dba_3/**1** as catalyst system, and aryl bromides and aryl chlorides as the two coupling substrates. The success of this reaction relies on the fact that the amination using an aryl bromide was completed in 2–3 h at 60–80 °C, whereas the aryl chlorides required a minimum of 110 °C to couple. In a typical procedure, the reaction of 4-aminostyrene with 1-bromo-4-*tert*-butyl benzene and 4-chlorotoluene afforded product **8a**. The reaction mixture was heated at 85 °C for 2 h, during which time monoamination was completed as judged by TLC. Raising the temperature to 110 °C for another 16 h completed the synthesis of **8a** in 80% yield (entry 1 in Table 4).

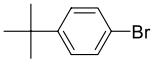
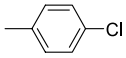
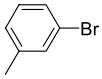
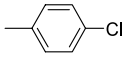
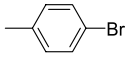
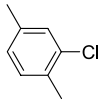
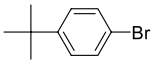
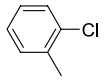
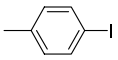
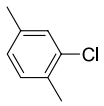
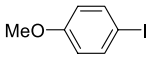
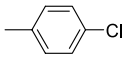
All the products in Table 4 are novel and their structures were assigned on the basis of their ^1H and ^{13}C NMR, and their HRMS spectra. As with other aryl chlorides, sterically hindered examples such as 2-chlorotoluene and 2-chloro-*p*-xylene were equally reactive, affording the coupled products in moderate to good yields (Table 4, entries 3–5) (Scheme 4).



i. $Pd_2(dba)_3$, **1** (4 mol %), NaO-*t*-Bu, dry toluene.

Scheme 4.

Table 4. One-pot synthesis of unsymmetrically substituted *N*,*N*-diarylaminostyrenes

Entry	Aryl halide (**3**)	Aryl halide (**4**)	Yield (%)[a,b]
1			80
2			81
3			66
4			53
5			73
6			68

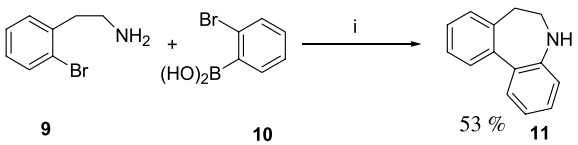
[a] Isolated yield, average of two runs.
[b] Reaction conditions: $Pd_2(dba)_3$ (2 mol%), **1** (4 mol%), NaO-*t*-Bu (2.5 equiv), aryl halide **3** (1 equiv), aryl halide **4** (1.2 equiv), 10 mL of dry toluene, 2 h at 85 °C and then the temperature was raised to 110 °C for 16 h, argon atmosphere.

2.5. Synthesis of 5,6-dihydro-7*H*-dibenz[*b*,*d*]azepine

To test a different application of proazaphosphatranes as ligands in one-pot multi-component reactions, we tried a one-pot amination/Suzuki sequence for the synthesis of 5,6-dihydro-7*H*-dibenz[*b*,*d*]azepine (**11**). Apart from an isolated literature report for the synthesis of **11** in 48% yield, via a trifluoromethanesulfonic acid-catalyzed cyclization of *N*-aminophenethylaniline,[20] no other descriptions for the synthesis of this compound were found in the literature. Although a single report of a one-pot amination/Suzuki reaction was found for the synthesis of 1,3-diphenylindazoles; this protocol required a bi-catalytic system.[21]

The reaction of 2-bromophenethylamine with 2-bromophenylboronic acid in the presence of 4 mol% of $Pd(OAc)_2$ and 8 mol% of **1** at 110 °C for 24 h afforded **11** in 53% isolated yield (Scheme 5).

Although, possible side reactions such as inter and intra molecular amination[22] and Suzuki coupling could be expected under our experimental conditions, we were able to isolate the expected product in somewhat better yield than that reported earlier.[20] The product was characterized by its ^1H and ^{13}C NMR and high-resolution mass spectra. Further elaboration of the methodology depicted in Scheme 5 to synthesize more complex molecules using one-pot sequential reactions is underway.



i. $Pd(OAc)_2$ (4 mol %), **1** (8 mol %), Cs_2CO_3 (4 equiv), 10 mL of dry toluene, 110 °C, 24 h., argon atmosphere.

Scheme 5.

3. Conclusion

The Pd_2dba_3/**1** ligand system has been shown to be useful for the one-pot synthesis of a variety of symmetrically and unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes and for *N*,*N*-diarylaminostyrenes. Interestingly, the same catalyst system is used for both the amination and the inter-molecular Heck coupling with a catalyst loading that is relatively low (2 mol% of $Pd_2(dba)_3$ and 4 mol% of the ligand). Using 4 mol% of $Pd(OAc)_2$ and 8 mol% of **1**, 5,6-dihydro-7*H*-dibenz[*b*,*d*]azepine was synthesized in moderate yield in a one-pot amination/Suzuki reaction.

4. Experimental

4.1. General considerations

All reactions were performed under an atmosphere of argon in oven dried glassware. Toluene was collected from a Grubbs type solvent purification system (Innovative Technologies) and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on Varian VXR 300 MHz and Bruker 400 MHz NMR spectrometers. NMR spectra were obtained using $CHCl_3$-*d* as solvent. Chemical shifts are given as δ values with tetramethylsilane or the $CHCl_3$ proton at 7.27 as the internal standard. Mass spectra were recorded on a Kratos MS-50 mass spectrometer.

4.2. General procedure for the synthesis of symmetrically substituted *N*,*N*-diarylaminostyrenes

An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with Pd_2dba_3 (2 mol%) and NaO*t*Bu (1.75 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. Ligand **1** (4 mol%), 4-aminostyrene (0.5 mmol), arylhalide **3** (1 mmol) and toluene (10 mL) were successively added

via syringe. The tube was heated at the temperature and for the time specified in Table 1, all the starting material was converted in to the corresponding *N*,*N*-dirylaminostyrenes as judged by TLC. To this reaction mixture, aryl halide **4** (0.6 mmol) was added and the temperature was raised to 110 °C. After heating for another 16 h, the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a short column of silica gel to remove the solid impurities and the filtrate was concentrated in vacuo. The crude products were purified by column chromatography using 0.5–2% EtOAc/hexane mixtures as eluants to afford the coupled products.

4.2.1. *N*,*N*-Diphenyl-4-[2-(4-methylphenyl)ethenyl]benzenamine. See Table 1, entry 1.[15]

4.2.2. *N*,*N*-Bis(4-methoxyphenyl)-4-[2-phenylethenyl] benzenamine. See Table 1, entry 2.[15]

4.2.3. *N*,*N*-Bis(3-methylphenyl)-4-[2-phenylethenyl]benzenamine. See Table 1, entry 3.[15]

4.2.4. *N*,*N*-Bis(4-methylphenyl)-4-[2-phenylethenyl]benzenamine. See Table 1, entries 4 and 8.[15]

4.2.5. *N*,*N*-Bis(3-methoxyphenyl)-4-[2-phenylethenyl] benzenamine. See Table 1, entry 5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 6H), 6.59–6.72 (m, 6H), 7.04–7.27 (m, 7H), 7.34–7.42 (m, 4H), 7.50 (d, J=7.32 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.48, 108.72, 110.42, 117.16, 124.24, 126.49, 127.32, 127.49, 128.31, 128.84, 130.03, 131.92, 137.75, 147.23, 148.81, 160.60. HRMS: calcd for $C_{28}H_{25}NO_2$ (M^+) 407.18853, found: 407.18903.

4.2.6. *N*,*N*-Bis(4-methoxyphenyl)-4-[2-(4-methylphenyl) ethenyl]benzenamine. See Table 1, entry 6.[15]

4.2.7. *N*,*N*-Bis(4-methoxyphenyl)-4-[2-(3-methylphenyl) ethenyl]benzenamine. See Table 1, entry 7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.81 (s, 6H), 6.84–6.96 (m, 7H), 7.02–7.10 (m, 6H), 7.24–7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.68, 55.67, 114.84, 120.64, 123.54, 126.26, 126.76, 127.04, 127.33, 128.06, 128.28, 128.68, 129.78, 137.88, 138.28, 140.89, 148.39, 156.03. HRMS: calcd for $C_{29}H_{27}NO_2$ (M^+) 421.20418, found:421.20489.

4.2.8. *N*-(4-Methylphenyl)-*N*-(phenyl)-4-[2-phenylethenyl]benzenamine. See Table 2, entries 1, 3, 5, and 7.[16]

4.2.9. *N*-(4-Methoxyphenyl)-*N*-(phenyl)-4-[2-phenylethenyl]benzenamine. See Table 2, entries 2 and 8.[9]

4.2.10. *N*-(4-Methoxyphenyl)-*N*-(4-methylphenyl)-4-[2-(4-methylphenyl)ethenyl]benzenamine. See Table 2, entry 4.[16]

4.2.11. *N*-(4-*tert*-Butyl-phenyl)-*N*-(phenyl)-4-[2-phenylethenyl]benzenamine. See Table 2, entry 6. Pd_2dba_3 (9.2 mg, 2.0 mol%), NaO*t*Bu (168 mg, 1.75 mmol), ligand **1** (6.8 mg, 4.0 mol%), 4-aminostyrene (59.5 mg, 0.499 mmol), 1-bromo-4-*tert*-butyl benzene (106.5 mg, 0.4997 mmol), and 10 mL of dry toluene was heated at 85 °C for 3 h and to the same reaction mixture iodobenzene (224.4 mg, 1.099 mmol) was added and heated at 110 °C for 16 h afforded the coupled product **6f** (143 mg, 71%) as a yellow solid after chromatography with 1% EtOAc/hexane mixtures as eluant.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (s, 9H), 6.90–7.02 (m, 9H), 7.12–7.28 (m, 9H), 7.37 (d, J=7.52 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.66, 34.54, 122.90, 123.41, 124.40, 124.47, 126.31, 126.46, 126.99, 127.39, 127.47, 128.43, 128.82, 129.37, 131.30, 137.85, 144.88, 146.29, 147.69, 147.83. HRMS: calcd for $C_{30}H_{29}N$ (M^+) 403.23000, found: 403.23052.

4.2.12. *N*-(3-Methoxyphenyl)-*N*-(phenyl)-4-[2-phenylethenyl]benzenamine. See Table 2, entry 9.[15]

4.2.13. *N*-(3-Pyridyl)-*N*-(phenyl)-4-[2-phenylethenyl] benzenamine. See Table 2, entry 10. Chromatography with 20–50% EtOAc/hexane mixture as eluants. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.94–7.03 (m, 8H), 7.18–7.33 (m, 8H), 7.39 (d, J=7.56 Hz, 2H), 8.13–8.14 (m, 1H), 8.31 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 124.12, 124.80, 126.51, 127.77, 128.82, 129.78, 132.72, 137.53, 143.34, 144.22, 145.44, 146.38, 146.71. HRMS: calcd for $C_{25}H_{20}N_2$ (M^+) 348.16265, found: 348.16317.

4.3. General procedure for the synthesis of unsymmetrically substituted *trans*-4-*N*,*N*-diarylaminostilbenes (different aryl groups on nitrogen)

An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with Pd_2dba_3 (2 mol%) and NaO*t*Bu (1.75 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. Ligand **1** (4 mol%), 4-aminostyrene (0.5 mmol), arylhalide **3** (1.1 mmol) and toluene (10 mL) were successively added via syringe. The tube was heated at the temperature and for the time specified in Table 1, the reaction mixture was cooled to room temperature. The reaction mixture was filtered through a short column of silica gel to remove the solid impurities and the filtrate was concentrated in vacuo. The crude products were purified by column chromatography using 0.5–2% EtOAc/hexane mixtures as eluant to afford the coupled products.

4.3.1. 4-Ethenyl-*N*,*N*-diphenylbenzenamine. See Table 3, entry 1.[17b]

4.3.2. 4-Ethenyl-*N*,*N*-bis(4-methylphenyl)benzenamine. See Table 3, entries 2 and 8.[17b]

4.3.3. 4-Ethenyl-*N*,*N*-bis(3-methylphenyl)benzenamine. See Table 3, entry 3.[19]

4.3.4. 4-Ethenyl-*N*,*N*-bis(3,5-dimethylphenyl)benzenamine. See Table 3, entry 4.[13]

4.3.5. 4-Ethenyl-*N*,*N*-bis(4-*tert*-butylphenyl)benzenamine. See Table 3, entry 5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 18H), 5.10 (d, J=10.89 Hz, 1H), 5.58 (d, J=17.58 Hz, 1H), 6.60 (dd, J_1=10.86 Hz, J_2=17.58 Hz, 1H), 6.99–7.03 (m, 6H), 7.24–7.27 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.66, 34.50, 111.81, 122.96, 124.19, 126.22,

127.10, 131.27, 136.55, 145.10, 145.92, 148.04. HRMS: calcd for $C_{28}H_{33}N$ (M^+) 383.26130, found: 383.26190.

4.3.6. 4-Ethenyl-*N*,*N*-bis(4-chlorophenyl)benzenamine. See Table 3, entry 6. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.15 (d, $J=10.86$ Hz, 1H), 5.61 (d, $J=17.58$ Hz, 1H), 6.59 (dd, $J_1=10.86$ Hz, $J_2=17.58$ Hz, 1H), 6.96–6.99 (m, 6H), 7.15–7.17 (m, 4H), 7.19–7.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.04, 124.16, 125.42, 127.49, 128.30, 129.64, 133.01, 136.18, 146.07, 146.81. HRMS: calcd for $C_{20}H_{15}NCl_2$ (M^+) 339.05816, found: 339.05855.

4.3.7. 4-Ethenyl-*N*,*N*-bis(1-naphthyl)benzenamine. See Table 3, entry 7.[19]

4.4. General procedure for the synthesis of unsymmetrically substituted *N*,*N*-diarylaminostyrenes

An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with Pd_2dba_3 (2 mol%) and NaO*t*Bu (1.75 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. Ligand **1** (4 mol%), 4-aminostyrene (0.5 mmol), arylbromide (0.5 mmol), aryl chloride (0.6 mmol) and toluene (10 mL) were successively added via syringe. The tube was heated at 85 °C for 2 h and then the temperature was raised to 110 °C for an additional 16 h. The reaction mixture was cooled to room temperature and filtered through a short column of silica gel to remove the solid impurities and the filtrate was concentrated in vacuo. The crude products were purified by column chromatography using hexane—1% EtOAc/hexane mixtures as eluant to afford the coupled products.

4.4.1. 4-Ethenyl-*N*-(4-methylphenyl)-*N*-(4-*tert*-butylphenyl)benzenamine. See Table 4, entry 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 9H), 2.31 (s, 3H), 5.10 (d, $J=10.98$ Hz, 1H), 5.58 (d, $J=17.58$ Hz, 1H), 6.60 (dd, $J_1=11.01$ Hz, $J_2=17.58$ Hz, 1H), 6.98–7.05 (m, 8H), 7.22–7.27 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.07, 31.66, 34.50, 111.80, 122.76, 123.89, 124.17, 125.07, 126.19, 127.08, 130.06, 131.19, 132.87, 136.50, 145.10, 145.28, 145.79, 148.04. HRMS: calcd for $C_{25}H_{27}N$ (M^+) 341.21435, found: 341.21500.

4.4.2. 4-Ethenyl-*N*-(4-methylphenyl)-*N*-(3-methylphenyl)benzenamine. See Table 4, entry 2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.34 (s, 3H), 5.13 (d, $J=10.98$ Hz, 1H), 5.61 (d, $J=17.70$ Hz, 1H), 6.62 (dd, $J_1=10.89$ Hz, $J_2=17.58$ Hz, 1H), 6.82–6.92 (m, 3H), 6.99–7.16 (m, 7H), 7.27–7.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.06, 21.62, 111.98, 121.47, 123.16, 123.74, 124.89, 125.19, 127.14, 129.18, 130.11, 131.45, 133.00, 136.49, 139.22, 145.28, 147.89, 148.00. HRMS: calcd for $C_{22}H_{21}N$ (M^+) 299.16740, found: 299.16778.

4.4.3. 4-Ethenyl-*N*-(4-methylphenyl)-*N*-(2,5-dimethylphenyl)benzenamine. See Table 4, entries 3 and 5. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 3H), 2.28 (s, 3H), 2.32 (s, 3H), 5.10 (d, $J=10.86$ Hz, 1H), 5.58 (d, $J=17.58$ Hz, 1H), 6.61 (dd, $J_1=10.86$ Hz, $J_2=17.58$ Hz, 1H), 6.85–7.07 (m, 8H), 7.12–7.15 (m, 1H), 7.24–7.27 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.33, 20.96, 21.06, 111.27, 120.36, 122.72, 127.05, 127.09, 129.87, 130.12, 130.15, 131.65, 133.36, 136.57, 137.23, 144.83, 145.18, 147.74. HRMS: calcd for $C_{23}H_{23}N$ (M^+) 313.18305, found: 313.18347.

4.4.4. 4-Ethenyl-*N*-(4-*tert*-butylphenyl)-*N*-(2-methylphenyl)benzenamine. See Table 4, entry 4. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (s, 9H), 2.05 (s, 3H), 5.09 (d, $J=10.89$ Hz, 1H), 5.57 (d, $J=17.61$ Hz, 1H), 6.60 (dd, $J_1=10.89$ Hz, $J_2=17.58$ Hz, 1H), 6.87–6.97 (m, 4H), 7.13–7.27 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.80, 31.65, 34.41, 111.36, 120.48, 122.04, 126.06, 126.22, 127.09, 127.54, 129.79, 130.29, 131.87, 136.55, 136.73, 144.59, 144.96, 145.42, 147.56. HRMS: calcd for $C_{25}H_{27}N$ (M^+) 341.21435, found: 341.21499.

4.4.5. 4-Ethenyl-*N*-(4-methylphenyl)-*N*-(4-methoxyphenyl)benzenamine. See Table 4, entry 6. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 3H), 3.69 (s, 3H), 5.00 (d, $J=8.10$ Hz, 1H), 5.48 (d, $J=13.17$ Hz, 1H), 6.50 (dd, $J_1=8.16$ Hz, $J_2=13.00$ Hz, 1H), 6.72–6.74 (m, 2H), 6.83–6.97 (m, 8H), 7.13–7.15 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.00, 55.65, 111.54, 114.86, 121.67, 124.22, 127.05, 127.16, 129.99, 130.64, 132.38, 136.46, 140.86, 145.43, 148.26, 156.18. HRMS: calcd for $C_{22}H_{21}NO$ (M^+) 315.16231, found: 315.16277.

4.4.6. 5,6-Dihydro-7*H*-dibenz[*b*,*d*]azepine (11). An oven dried Schlenk tube equipped with a magnetic stirring bar was charged with $Pd(OAc)_2$ (4.48 mg, 3.99 mol%), Cs_2CO_3 (652 mg, 2.00 mmol) and 2-bromophenylboronic acid (100 mg, 0.497 mmol). The tube was capped with a rubber septum, evacuated and then flushed with argon three times. Ligand **1** (13.68 mg, 7.988 mol%), 2-bromophenethylamine (100 mg, 0.499 mmol) and toluene (10 mL) were successively added via syringe. The tube was heated at 110 °C for 24 h. Then the reaction mixture was cooled to room temperature and filtered through a short column of silica gel to remove the solid impurities and then the filtrate was concentrated in vacuo. The crude product was purified by column chromatography using hexanes as eluant to afford the **11** (51 mg, 53%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.13 (t, $J=8.4$ Hz, 2H), 3.95 (t, $J=8.4$ Hz, 2H), 6.75 (t, $J=7.32$ Hz, 1H), 6.96–7.00 (m, 1H), 7.09–7.11 (m, 1H), 7.16 (t, $J=8.6$ Hz, 2H), 7.24–7.27 (m, 2H), 7.34–7.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.37, 52.27, 108.27, 117.80, 118.98, 121.06, 125.20, 127.22, 129.31, 131.42, 144.28. HRMS: calcd for $C_{14}H_{13}N$ (M^+) 195.10480, found: 195.10506.

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