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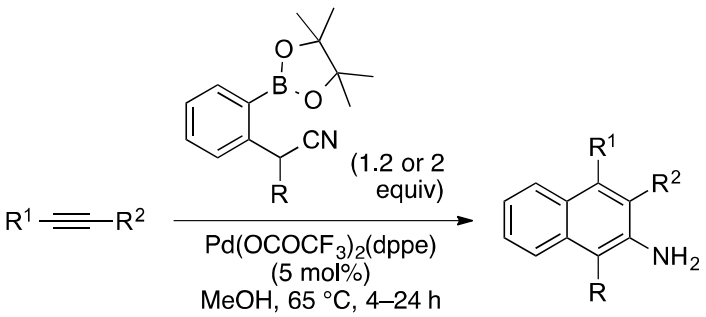
TOC



ABSTRACT

1,2-Bis(diphenylphosphino)ethane (dppe)-ligated palladium(II) complexes catalyze the annulation of internal alkynes with 2-(cyanomethyl)phenylboronates to provide 3,4-disubstituted-2-naphthalenamines in good yields. The annulation reaction proceeds under mild and neutral conditions and requires methanol as an essential solvent. In addition to symmetrical alkynes, unsymmetrical ones substituted by aryl, alkyl, and alkynyl groups participate in the annulation to

afford the corresponding 2-naphthalenamines with electron-withdrawing sp^2- and sp-carbons preferentially located at the C-3 position. Substituents including an alkyl or alkoxy group on the cyanomethyl moiety and a halogen atom on the benzene ring in the boronates are compatible with the reaction conditions. The annulation proceeds through the transmetalation of the palladium(II) complexes with the boronates and alkyne insertion followed by nucleophilic addition of the generated alkenylpalladium(II) species to the intramolecular cyano group. Stoichiometric reactions revealed that the methanol solvent was effective for both transmetalation and catalyst regeneration.

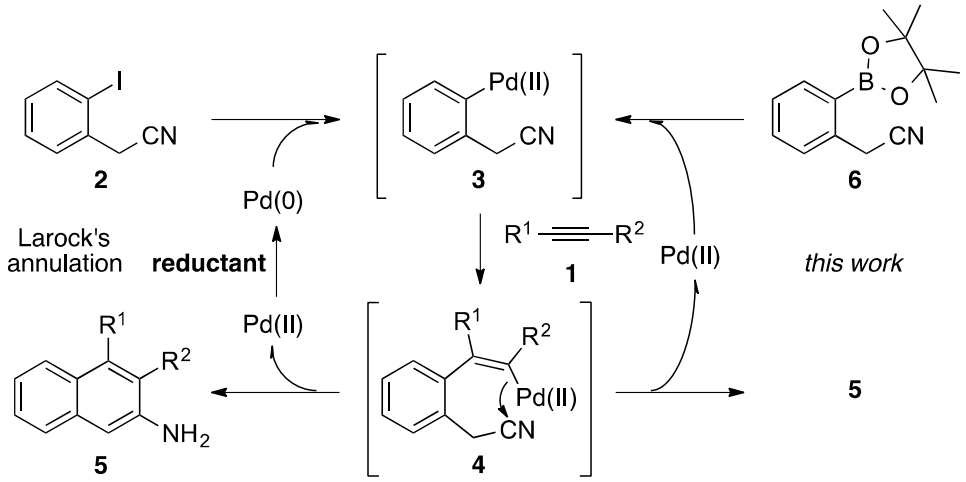
INTRODUCTION

Naphthalenamines and their derivatives are an important class of compounds due to their biological activity[1], which includes emetic, spasmolytic, and antimicrobacterial activity; they are also known for their utility as starting materials for azo dyes.[2] Moreover, their homo- and hetero-dimers [i.e., 1,1′-binaphthyl-2,2′-amines (BINAMs)] have recently received considerable attention as axially chiral ligands, organocatalysts, and reagents.[3] The introduction of substituents in the 3- and 3′-positions of BINAM can improve the enantioselectivities of reactions; however, these syntheses are not trivial in comparison with those of the corresponding alcohols (BINOLs) and phosphines (BINAPs).[4, 5] Unsubstituted and substituted BINAMs can be synthesized by the oxidative coupling of the parent 2-naphthalenamines.[6, 7] Some conventional methods including the Bucherer reaction of naphthols,[8] the Curtius rearrangement of naphthoic acids,[9] the Beckmann rearrangement of acetonaphthone oximes,[10] and transformation of tetralone derivatives can synthesize 2-naphthalenamines.[11] However, the poor availability of the starting bicyclic compounds (especially multi-substituted ones) and harsh reaction conditions render them neither practical nor applicable to substrates, including a wide variety of functional groups. There is still a need to develop an efficient method to prepare substituted 2-naphthalenamines.

A decade ago, Larock developed a method for synthesizing 2-naphthalenamines **5** based on the annulation of alkyne **1** with 2-iodophenylacetonitrile (**2**) (Scheme 1, clockwise cycle on the left).[12] The reaction is thought to proceed through the oxidative addition of **2** to in situ-generated

palladium(0), alkyne insertion between the aryl-palladium bond in **3**, and nucleophilic addition of alkenylpalladium(II) **4** to the proximal nitrile followed by aromatization. An additional step (i.e., reduction of the (amido)palladium(II) complex formed in the final step of the catalytic cycle with triethylamine) is also essential to regenerate palladium(0). The annulation reaction offers relatively mild reaction conditions and provides a wide variety of 3,4-disubstituted-2-naphthalenamines **5**. However, the method still requires a high reaction temperature (100 °C), long reaction time (48 h), and excess alkyne (3 equiv) along with additives. Moreover, the reluctant reduction step sometimes causes oxidation of the annulation products with an alkyl substituent at C-3 along with the incorporation of the iminium salt formed by the oxidation of triethylamine into the products.

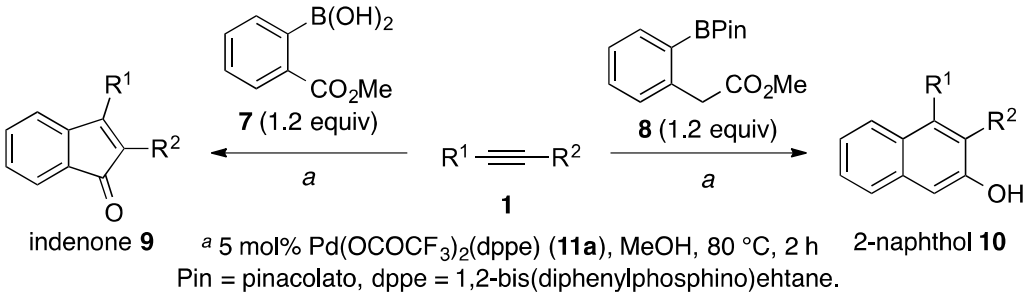
Scheme 1. Annulation of internal alkyne **1** with 2-iodo- and 2-borono-phenylacetonitriles **2** and **6**



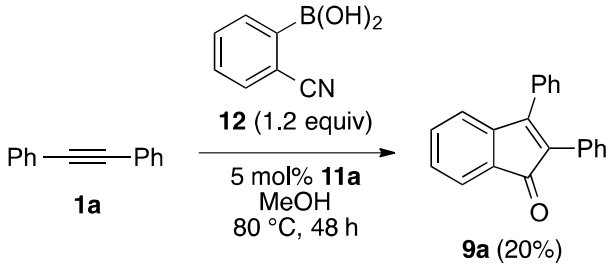
Previously, we reported the palladium(II)-catalyzed annulation of internal alkynes with 2-(methoxycarbonyl)phenylboronic acid (**7**) and 2-[(methoxycarbonyl)methyl]phenylboronate **8,** leading to 2,3-disubstituted 1*H*-indenones **9** and 3,4-disubstituted 2-naphthols **10**, respectively (Scheme 2).[13] The annulation proceeds through aryl-palladium(II) intermediates generated by transmetalation between the arylboron reagents and palladium(II) catalyst and requires no redox step. In contrast to the successful Larock's annulation of diphenylacetylene (**1a**) with *o*-iodobenzonitrile, leading to indenone **9a**,[12a, 14] the substitution of the methoxycarbonyl group in boronic acid **7** by a cyano group caused a significant decrease in the yield of **9a** (Scheme 3).[13–15] The

result makes us hesitant to test the homologue 2-(cyanomethyl)phenylboronate **6** for the preparation of 2-naphthalenamines **5** (Scheme 1, counter-clockwise cycle on the right), although there are several reports on palladium-catalyzed reactions with nitrile electrophiles.[16-20] Furthermore, similar dppe-ligated cationic palladium(II) catalysts were reported to promote the hydroamination of **1a** with aromatic amines.[21] Herein, we have reported the successful synthesis of palladium(II)-catalyzed 3,4-disubstituted 2-naphthalenamines **5** based on the annulation of internal alkynes **1** with commercially available[22] or readily accessible boronate **6**.

Scheme 2. Pd(II)-catalyzed annulation of **1** with *ortho*-ester-containing phenylboron reagents **7** and **8**



Scheme 3. Unsuccessful Pd(II)-catalyzed annulation of **1a** with 2-cyanophenylboronic acid (**12**)

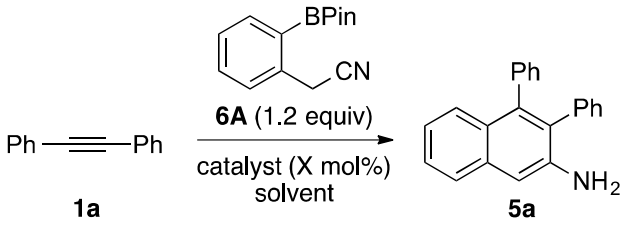


RESULTS AND DISCUSSION

Reaction Optimization and Substrate Scope. In contrast to the ineffective annulation with 2-cyanophenylboronic acid (**12**), the reaction of **1a** with 1.2 equiv of 2-(cyanomethyl)phenylboronate **6A** under 5 mol% $Pd(OCOCF_3)_2(dppe)$[23] (**11a**, dppe = 1,2-bis(diphenylphosphino)ethane) catalyst in

methanol upon heating at 80 °C for 3 h led to the formation of 3,4-diphenyl-2-naphthalenamine (**5a**) in high yield (Table 1, entry 1). As with the previously reported synthesis of 2-naphthols,[13] methanol turned out to be the best solvent for the annulation, and aprotic solvents were much less effective (entries 1 vs. 2–5). The protic solvent should play an important role in the annulation. It is noteworthy that the hydroamination of **1a** with in situ-formed **5a** did not take place under the reaction conditions.[21] Reducing the reaction temperature to 65 °C did not affect the yield of **5a** (entry 6), while a lower catalyst loading of **11a** gave **5a** in much poorer yield (entries 6 vs. 7). In contrast, the amount of cationic palladium(II) complex **11b**[24] can be reduced to 2 mol% without a significant decrease in product yield (entries 8 and 9).

Table 1. Optimization of Pd(II)-catalyzed annulation of **1a** with **6A**

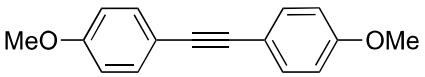
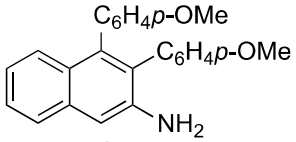
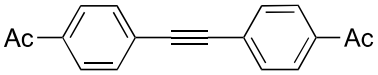
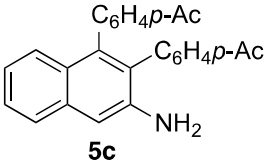
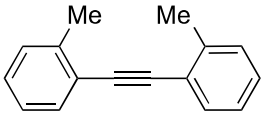
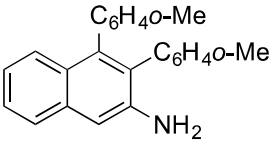
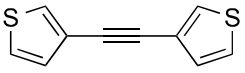
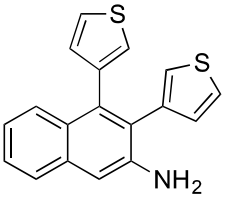
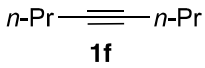
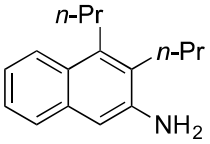
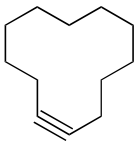
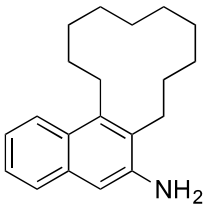
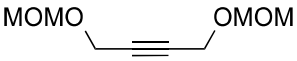
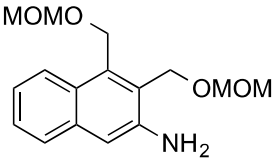
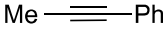
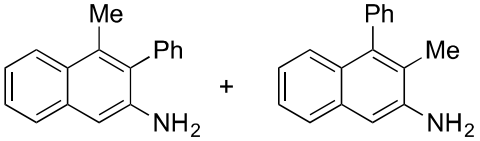


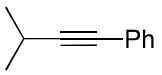
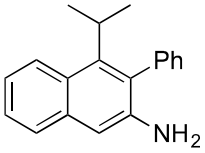
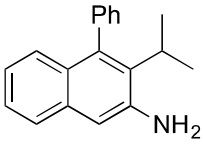
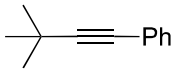
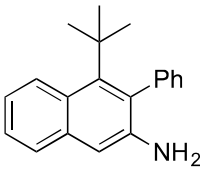
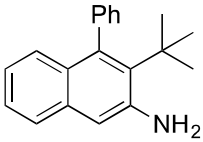
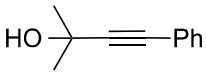
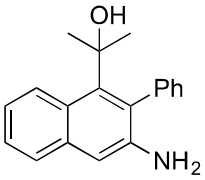
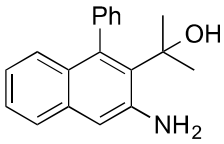
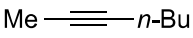
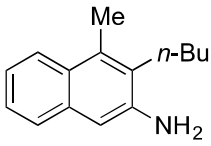
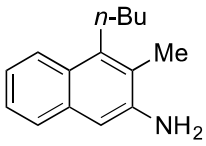
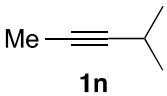
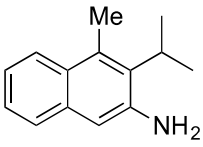
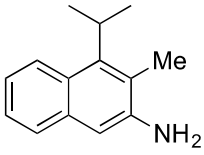
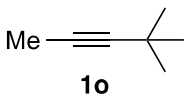
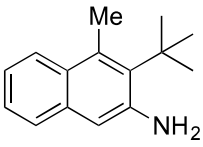
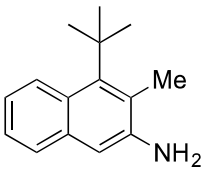
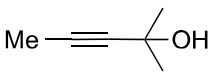
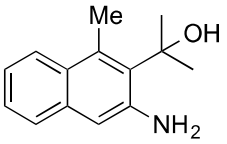
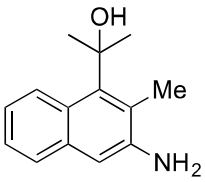
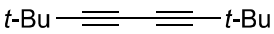
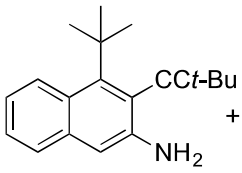
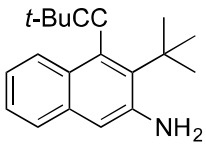
entry	catalyst	X	solvent	temp (°C)	time (h)	yield (%)
1	$Pd(OCOCF_3)_2$(dppe) (**11a**)	5	MeOH	80	3	88
2	**11a**	5	DMF	80	24	10
3	**11a**	5	acetone	80	24	6
4	**11a**	5	CH_3CN	80	12	5
5	**11a**	5	1,4-dioxane	80	12	<2
6	**11a**	5	MeOH	65	4	89
7	**11a**	2	MeOH	65	24	57
8	$[Pd(PhCN)_2(dppe)](BF_4)_2$ (**11b**)	5	MeOH	65	2	99
9	**11b**	2	MeOH	65	6	94

With readily available catalyst **11a**, the annulation reactions using various alkynes **1b–q** were examined (Table 2). Symmetrical diarylacetylenes **1b** and **1c** with electron-donating or electron-

withdrawing substituents at the *para*-positions were converted into 3,4-diaryl-2-naphthalenamines **5b** and **5c**, respectively, in high yields (entries 1 and 2). While the yield of the annulation product **5d** obtained from *ortho*-substituted diarylacetylene **1d** was comparable to those of **5b** and **5c** (entry 3), the use of di(heteroaryl)alkyne **1e** resulted in slightly lower yield of **5e** (entry 4). The annulation of both acyclic and cyclic symmetrical dialkyl-substituted alkynes **1f** and **1g** afforded 3,4-dialkyl-2-naphthalenamines **5f** and **5g**, respectively, without any oxidation of the products[14a] (entries 5 and 6). Protected 1,4-butanediol **1h** also participated in the annulation to give naphthalenamine **5h** in moderate yield (entry 7). 2-Alkyl-substituted 1-phenylacetylenes **1i–k** underwent the annulations with **6A** to provide 4-alkyl-3-phenyl-2-naphthalenamines **5i–k** together with a small amount of 3-alkyl-4-phenyl-2-naphthalenamines **5i–k′** as a separable mixture (entries 8–11). The regioselectivity observed in the annulation of 1-phenyl-1-propyne (**1i**) with **6A** is similar to that of the palladium(II)-catalyzed annulation with **7**, leading to indenone **9**.[13] The secondary and tertiary alkyl groups in **1j** and **1k** lower the selectivity, preferring 3-phenyl-2-naphthalenamines (entries 9, 10 vs. 8). The tertiary alcohol in **1l** was compatible with the annulation conditions and competed with the phenyl group for the 3-position of the naphthalenamines to give **5l** and **5l′** in nearly equal amounts (entry 11). The annulation of 2-propynes **1m** and **1n** substituted by either primary or secondary alkyl groups furnished a mixture of two possible 2-naphthalenamines; the quantity of the formed 4-methyl substituted one was slightly more than that of the formed 3-methyl substituted one (entries 12 and 13). As in entries 10 and 11, the sterically similar *tert*-butyl and 2-hydroxypropan-2-yl groups in **1o** and **1p** guided the annulation in a different way and were preferentially incorporated in the C-4 and C-3 positions of the products, respectively (entries 14 and 15). It is worth noting that the regioselectivity of our annulation using 1,3-diyne **1q** is opposite to that of Larock's annulation with 2-iodophenylacetonitrile **2**, leading to the exclusive formation of **5q′** (entry 16).[12, 14] Unfortunately, the annulation reactions of alkynyl esters, alkynylsilanes, and terminal alkynes were unsuccessful. The structures of naphthalenamines prepared by our reactions with unsymmetrical alkynes **1i–q** were determined by NOESY correlation between the proton at C-5 and the protons of the substituent at C-4 in 2-aminonaphthanlenes **5i–q** and **5i–q′** (see Supporting Information).

Table 2. Annulation of symmetrical and unsymmetrical alkynes **1b–q** with **6A**[a]

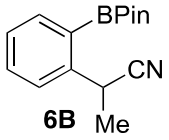
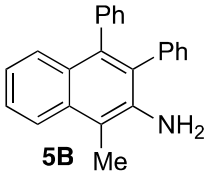
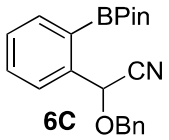
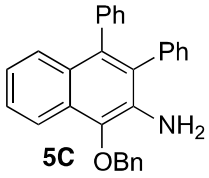
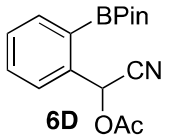
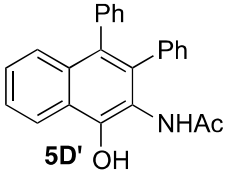
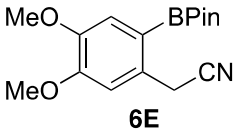
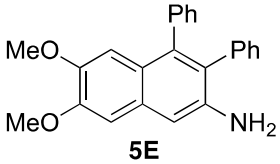
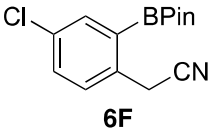
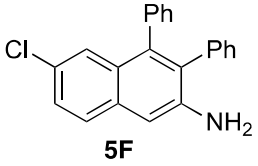
entry	alkyne **1**	product **5**	yield (%)
1	 **1b**	 **5b**	70
2	 **1c**	 **5c**	74
3	 **1d**	 **5d**	70
4	 **1e**	 **5e**	51
5	 **1f**	 **5f**	71
6	 **1g**	 **5g**	51
7	 **1h**	 **5h**	50
8	 **1i**	 **5i** **5i'**	**5i**: 73 **5i′**: 15

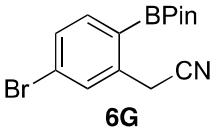
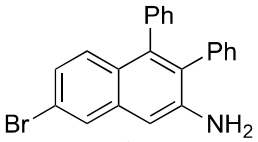
9	 **1j**	 **5j** +	 **5j'**	**5j**: 70 **5j′**: 27
10	 **1k**	 **5k** +	 **5k'**	**5k**: 33 **5k′**: 12
11	 **1l**	 **5l** +	 **5l'**	**5l**: 36 **5l′**: 33
12	 **1m**	 **5m** +	 **5m'**	**5m**: 40 **5m′**: 33
13	 **1n**	 **5n** +	 **5n'**	**5n**: 50 **5n′**: 33
14	 **1o**	 **5o** +	 **5o'**	**5o**: 22 **5o′**: 41
15	 **1p**	 **5p** +	 **5p'**	**5p**: 50 **5p′**: 23
16	 **1q**	 **5q** +	 **5q'**	**5q**: 77 **5q′**: 3

[a] Reaction conditions: **1b–q** (1 equiv), **6A** (1.2 equiv) and $Pd(OCOCF_3)_2$(dppe) (5 mol%), MeOH (0.4 M for **1b–q**), 65 °C, 4 h.

The effects of substituents in the boronate **6** on the annulation of **1a** were also examined. Methyl substitution on the cyanomethyl moiety in **6** did not hamper the annulation, which gave 1-methyl-3,4-diphenyl-2-naphthalenamine (**5B**) in 80% yield (Table 3, entry 1). The annulations of **1a** with benzyl- and acetyl-protected cyanohydrins **6C** and **6D** afforded 2-amino-1-naphthyl benzyl ether **5C** and 2-acetamido-1-naphthol **5D′** in excellent yields, respectively (entries 2, 3). The latter product **5D′** resulted from the annulation followed by *O*–*N* acyl migration instead of oxazole formation[12b]. Electron-donating methoxy groups and electron-withdrawing halogen atoms on the benzene ring in **6** did not affect the reactions, which gave **5E–G** in high yields (entries 4–6). The compatibility of halogen atoms in the palladium(II)-catalyzed reaction allows the further transformation of the halogen-containing products under palladium(0) catalysis.

Table 3. Annulation of **1a** with boronates **6B–G**[a]

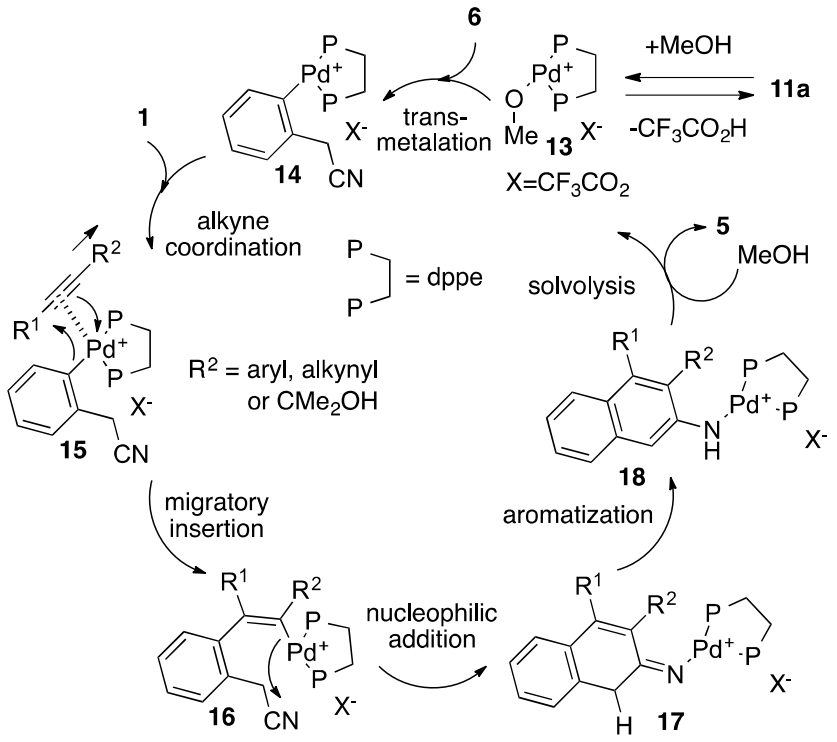
entry	boronate **6**	product **5**	yield (%)
1[b]	 **6B**	 **5B**	80
2[b]	 **6C**	 **5C**	91
3[b]	 **6D**	 **5D'**	92
4[c]	 **6E**	 **5E**	81
5[c]	 **6F**	 **5F**	83

6[c]	 **6G**	 **5G**	78

[a] Reaction conditions: **1a** (1 equiv), **6** (2 equiv for **6B–D**, 1.2 equiv for **6E–G**) and $Pd(OCOCF_3)_2$(dppe) (5 mol%), MeOH (0.4 M for **1a**), 65 °C. [b] Reaction for 24 h. [c] Reaction for 4 h.

Reaction Mechanism. A plausible reaction mechanism is shown in Scheme 4. Methanol is an essential solvent for the annulation and converts catalyst **11a** into the corresponding methoxo-complex **13**[25] along with trifluoroacetic acid, the former of which should be favorable for transmetalation with arylboronate **6** to give aryl-palladium(II) species **14**.[26] The migratory insertion of coordinated alkyne **1** between the aryl-palladium bond in **15** is accelerated and guided by the substituent with electron-withdrawing sp^2- and sp-carbons or a 1-hydroxyalkyl group[27] as R^2. The nucleophilic addition of alkenyl-palladium **16** to the proximal nitrile followed by the aromatization of **17** and solvolysis of amido complex **18** form naphthalenamine **5**, as well as catalyst **13**. Hence, the protic solvent would participate in the formation of (methoxo)palladium **13** not only from **11a** but also from **18**.

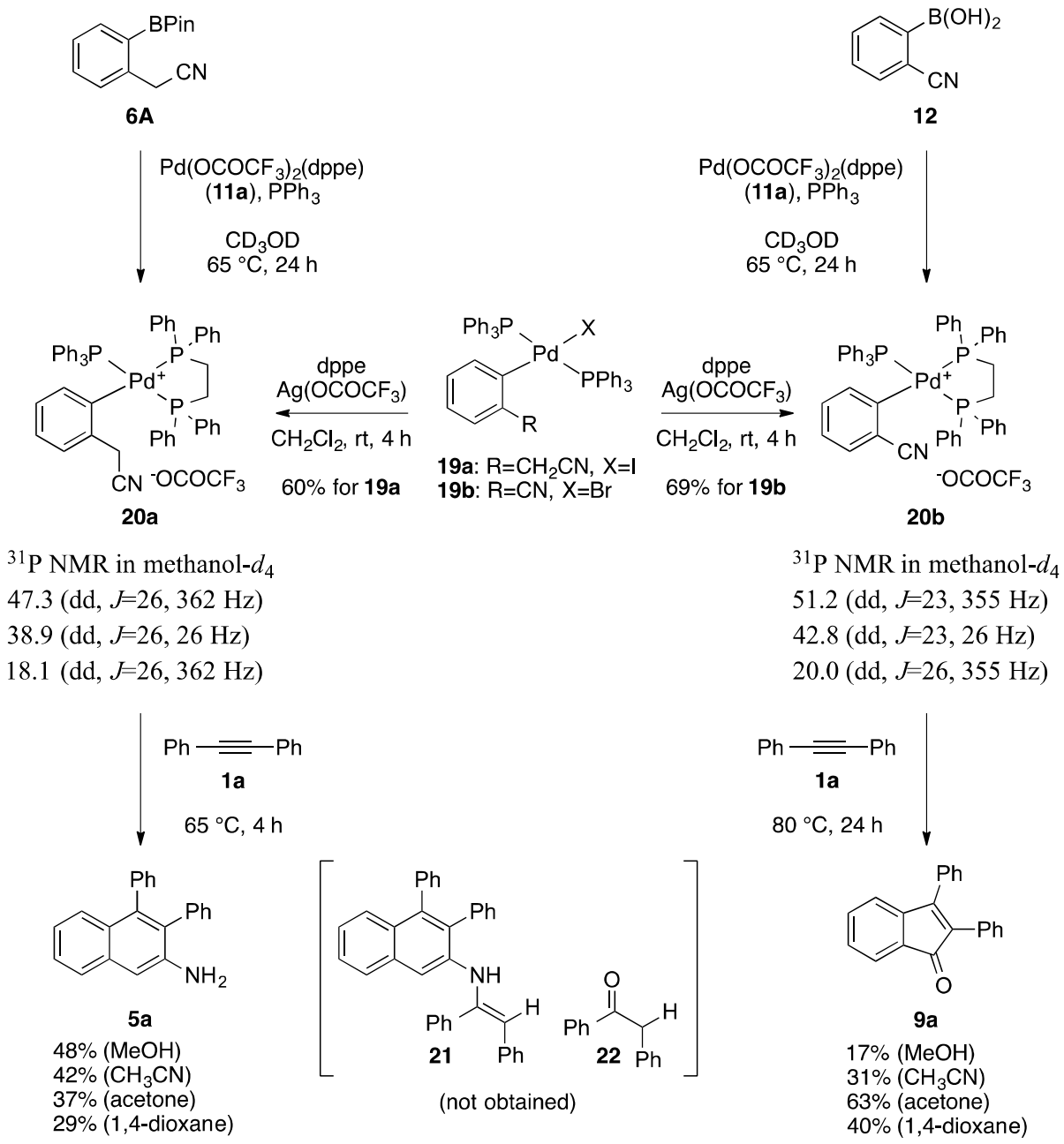
Scheme 4. Plausible reaction mechanism for the annulation



To verify the actual role of methanol in the catalytic cycle, the stoichiometric reactions shown in Scheme 5 were investigated. First, the solvent effect on the transmetalation reaction between dppe-ligated palladium **11a** and arylboronate **6A** in the presence of triphenylphosphine to stabilize the complex[28] was examined by ^{1}H and ^{31}P NMR experiments. Among the tested deuterium solvents (i.e., chloroform-*d*, acetonitrile-d_3, acetone-d_6, and methanol-d_4) only methanol-d_4 allowed the formation of palladium(II) complex **20a** after heating the mixture at 65 °C for 24 h.[29] The ^{31}P signals exhibited at 47.3 ppm (dd, J = 26, 362 Hz), 38.9 ppm (dd, J = 26, 26 Hz), and 18.1 ppm (dd, J = 26, 362 Hz) were identical to those of an authentic sample synthesized according to Miyaura's procedure[28] from silver trifluoroacetete, dppe, and bis(triphenylphosphine) complex **19a**, which was prepared by the oxidative addition of 2-iodophenylacetonitrile (**2**) to tetrakis(triphenylphosphine)palladium(0).[29] Similarly, the formation of lower homologue **20b** was also observed after heating a mixture of **11a**, *o*-cyanophenylboronic acid (**12**), and triphenylphosphine in methanol-d_4 under the same conditions.

Next, the stoichiometric annulation between diphenylacetylene (**1a**) and dppe-ligated arylpalladium complex **20a** was explored (Scheme 5). The annulation reaction of **20a** proceeded in acetonitrile, acetone, and 1,4-dioxane as well as in methanol, indicating that neither alkyne insertion nor nucleophillic addition to the adjacent nitrile in the catalytic cycle was affected by the solvent. The similar phenomena were also observed in the absence of the triphenylphosphine ligand (vide infra, Scheme 6. The yields of **5a** based on arylpalladium iodide **23a** were constant without regard to the solvents, i.e., methanol and acetonitrile). Even in the presence of excess **1a**, hydroamination products **21** and **22** were not observed. In contrast, methanol was much less effective than other solvents in the annulation of lower homologue **20b**, leading to indenone **9a**. The incompatibility of this step with methanol as solvent accounts for the inefficient annulation of **1a** with **12**.

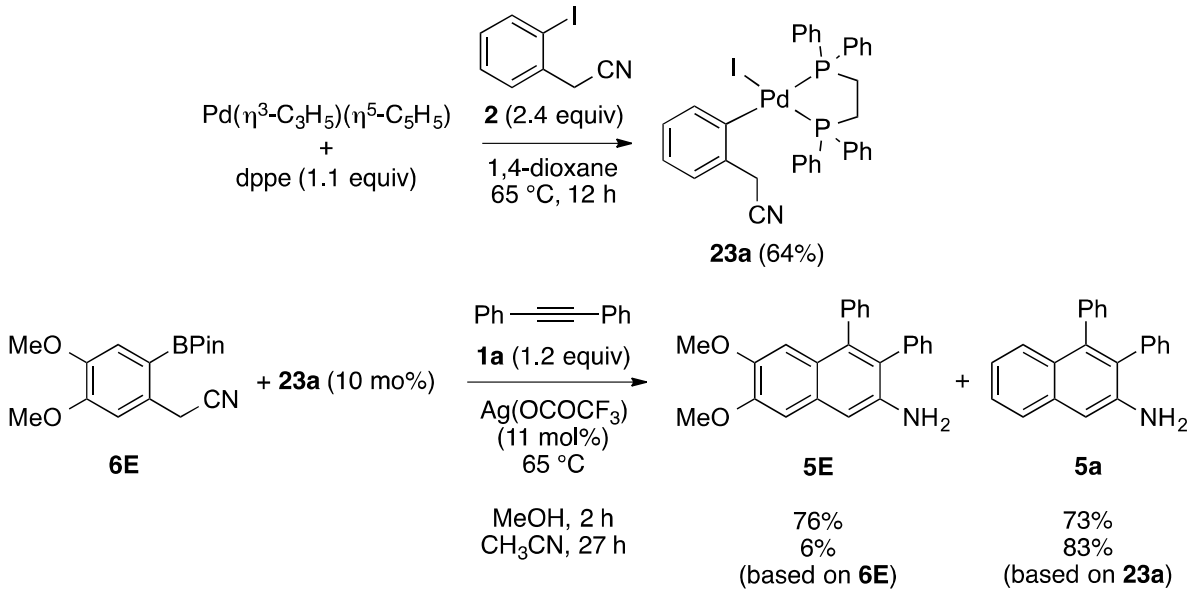
Scheme 5. Preparation of arylpalladiums **20a, b** via transmetalation of **11a** with **6A** and **12** and their annulation with **1a**



Finally, the solvent effect on the annulation between **1a** and **6E** in the presence of a catalytic amount of cationic dppe-ligated arylpalladium **15** (Scheme 4) generated in situ from arylpalladium iodide **23a** and silver trifluoroacetate was investigated to obtain insights into the catalyst regeneration step (Scheme 6). The palladium complex **23a** was easily prepared by the oxidative addition of 2-iodophenylacetonitrile (**2**) to the in situ-generated palladium(0)-dppe complex upon

heating in 1,4-dioxane.[31] While naphthalenamine **5a** derived from catalyst **23a** was obtained in comparable yields in methanol and acetonitrile, the yield of **5E** from boronate **6E** dramatically depended on the solvent (76% in methanol vs. 6% in acetonitrile). These contrasting results demonstrate that methanol is essential for the turnover (i.e., solvolysis) of amidopalladium **18** (Scheme 4).

Scheme 6. Preparation of **23a** and its catalytic use for the annulation between **1a** and **6E**



CONCLUSIONS

In summary, we have developed a new preparative method for 3,4-disubstituted-2-naphthalenamines based on the palladium(II)-catalyzed annulation of internal alkynes with 2-(cyanomethyl)phenylboronates. Compared with the palladium(0)-catalyzed reaction with (2-iodophenyl)acetonitrile, our naphthalenamine synthesis has the advantages of relatively low reagent consumption, lower reaction temperature, shorter reaction time, and wider substrate scope.[12] Moreover, our redox-free system did not cause product oxidation, which was sometimes observed in the former reaction. Investigations of annulations with functionalized phenylboronic acids leading to other carbo- and heterocycles and their asymmetric processes are underway in this laboratory.

EXPERIMENTAL SECTION

General Techniques. All commercially available reagents and anhydrous solvents including 1,4-dioxane, acetone, tetrahydrofuran (THF), dichloromethane, and benzene were purchased and used without further purification. Anhydrous methanol (MeOH) was obtained by distillation from magnesium. Anhydrous *N*, *N*-dimethylformamide (DMF) and acetonitrile were obtained by distillation from calcium hydride. All reactions were monitored by thin layer chromatography (TLC) performed on 0.25 mm silica gel glassplates (60 F_{254}) using UV light and ethanolic *p*-anisaldehyde-sulfuric acid, ethanolic molybdatophosphoric acid, aqueous cerium sulfate-hexaammonium heptamolybdate-sulfuric acid, or aqueous potassium permanganate-potassium carbonate-sodium hydroxide solutions as visualizing agents. Flash column chromatography was carried out with silica gel (spherical, neutral, 63-210 μm grade). Purifications of 2-naphthalenamines were performed on 0.75 mm PLC plates and 0.5 mm NH_2 silica gel 60 F_{254} Plates. Yields refer to chromatographically and spectroscopically homogenous materials. Melting points were measured on a melting point apparatus and were uncorrected. Only the strongest and/or structurally important absorptions of infrared (IR) spectra are reported in reciprocal centimeters (cm^{-1}). ^{1}H NMR spectra (400 MHz and 600 MHz), $^{13}C\{^{1}H\}$NMR spectra (100 MHz and 151 MHz), $^{31}P\{^{1}H\}$NMR spectra (243 MHz), and ^{19}F NMR spectra (564 MHz) were recorded in the indicated solvent. Chemical shifts (δ) are reported in delta (δ) units, parts per million (ppm). Chemical shifts for ^{1}H NMR spectra are given relative to signals for internal tetramethylsilane (0 ppm) or residual nondeuterated solvents, i.e., chloroform (7.26 ppm), acetone (2.04 ppm), acetonitrile (1.93 ppm), and methanol (3.30 ppm). Chemical shifts for ^{13}C NMR spectra are given relative to the signal for chloroform-*d* (77.0 ppm). Chemical shifts for ^{31}P NMR spectra are given relative to the signal for external 85% phosphoric acid (0 ppm). Chemical shifts for ^{19}F NMR spectra are given relative to the signal for external fluorobenzene (–113.8 ppm[32] in acetone-d_6). Multiplicities are reported by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), br–s (broad singlet). Coupling constants (*J*) are represented in hertz (Hz). ^{1}H and ^{13}C NMR chemical shifts were

assigned using a combination of COSY, NOESY, HMQC, and HMBC. Low and high-resolution mass spectra were measured on TOF-MS with EI, FAB, or ESI probe.

Materials. All internal alkynes are literature-known. Internal alkynes **1a**, **1f**, **1i**, **1m**, **1n**, **1o**, **1p** and **1q** were purchased. Arylacetylenes **1b**,[33] **1c**,[34] **1d**,[35] **1e**,[36] **1j**,[37] **1k**,[38] and **1l**[39] were prepared by Sonogashira reaction between the parent iodoarene and alkyne. Dialkyl acetylenes **1g**[40] and **1h**[41] were prepared according to the literature procedures. Catalysts **11a**[23] and **11b**[24] were prepared according to the literature procedures. *Trans*-[Pd{C_6H_4(CN)-2}Br(PPh_3)$_2$] (**19b**)[42] was prepared according to the literature procedure.

Preparation of 2-(cyanomethyl)phenylboronic acid pinacol ester: The boronates **6A–E** were prepared by borylation of the parent iodides according to the literature procedure.[43] The starting iodides except for 2-(benzyloxy)-2-(2-iodophenyl)acetonitrile and 2-(5-bromo-2-iodophenyl)acetonitrile were prepared according to the literature procedures.[44]

2-(Benzyloxy)-2-(2-iodophenyl)acetonitrile: To a solution of 2-iodobenzaldehyde[45] (1.08 g, 4.65 mmol) in benzyloxytrimethylsilane (1.86 g, 10.3 mmol) was added iron(III) chloride (15.1 mg, 93.1 μmol) at 0 °C.[46] After being stirred at 0 °C for 2 h, the mixture was treated with trimethylsilyl cyanide (0.70 mL, 5.6 mmol). The resulting mixture was stirred at 0 °C for 4 h and then partitioned between CH_2Cl_2 and phosphate buffer (pH 7). The aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography eluting with 20% EtOAc/hexane to yield the title compound (619 mg, 1.77 mmol, 38%) as a pale yellow oil.

R_f=0.55 (25% EtOAc/hexane). IR ν (neat, cm^{-1}): 3032, 2870, 1456, 1066, 1015, 753, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.73–7.34 (m, 6H), 7.11 (dd, *J* = 8.0, 7.2 Hz, 1H), 5.45 (s, 1H), 4.88 (d, *J* = 11.2 Hz, 1H), 4.74 (d, *J* = 11.2 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.0, 136.1, 135.5, 131.4, 129.2, 128.9, 128.7, 128.6, 128.65, 128.62, 116.8, 98.1, 73.9, 72.6. LRMS (EI) *m/z* (relative intensity) 349 $[M]^+$ (46), 243 (57), 242 (27), 116 (63), 92 (92), 91 (100). HRMS (EI, $[M]^+$): calcd for $C_{15}H_{12}INO$, 348.9964; found 348.9953.

2-(5-Bromo-2-iodophenyl)acetonitrile: To a solution of 5-bromo-2-iodobenzoic acid (981 mg, 3.00 mmol) in anhydrous THF (6.0 mL) was added borane-tetrahydrofuran complex (1 M, 9.0 mL, 9.0 mmol) at room temperature. After being refluxed for 2 h with stirring, the resulting mixture was cooled to 0 °C, cautiously treated with MeOH, and concentrated *in vacuo*. To a solution of the crude alcohol (960 mg) in anhydrous DCM (7.5 mL) were added anhydrous DMF (0.36 mL, 4.7 mmol) and thionyl chloride (0.44 mL, 6.0 mmol) successively at 0 °C. The mixture was stirred at room temperature for 1 h, and then treated with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with Et_2O twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. To a solution of the crude chloride (972 mg) in anhydrous DMF (9.0 mL) was added potassium cyanide (586 mg, 9.00 mmol) at room temperature. The mixture was stirred at 50 °C for 1 h, and then treated with water. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel chromatography eluting with 20% EtOAc/hexane to yield the title compound (476 mg, 1.48 mmol, 49% over three steps) as a colorless oil.

R_f=0.53 (25% EtOAc/hexane). IR ν (neat, cm^{-1}): 2925, 2243, 1457, 1398, 1012, 819. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.6 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.19 (dd, J = 8.6, 2.0 Hz, 1H), 3.79 (2H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.9, 135.2, 133.1, 132.0, 123.2, 116.5, 96.8, 29.7. LRMS (EI) *m/z* (relative intensity) 323 $[M+2]^+$ (98), 321 $[M]^+$ (100), 242 (18), 196 (27), 194 (27), 169 (17), 167 (17). HRMS (EI, $[M]^+$): calcd for C_8H_5NBrI, 320.8650; found 320.8641.

General procedure for the preparation of 2-(cyanomethyl)phenylboronic acid pinacol ester: To a mixture of 2-(2-iodophenyl)acetonitrile (1 equiv), triethylamine (3 equiv), 2-(dicyclohexylphosphino)biphenyl (4 mol%) and palladium diacetate (2 mol%) in anhydrous 1,4-dioxane (0.4 M for 2-(2-iodophenyl)acetonitrile) was added pinacolborane (4 equiv) at room temperature. After being stirred at 80 °C for 30 min, the resulting mixture was cooled to room temperature and cautiously treated with saturated aqueous NH_4Cl. The aqueous layer was extracted with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and

concentrated *in vacuo*. The product was purified by silica gel chromatography eluting with 20% EtOAc/hexane, unless otherwise noted.

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (6A)[43a]: Synthesis according to the general procedure from 2-(2-iodophenyl)acetonitrile[44a] (2.98 g, 12.3 mmol). Yield 85% (2.56 g, 10.5 mmol), dark orange oil. All the analytical data were in good agreement with values reported in the literature.[43a]

2-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanenitrile (6B): Synthesis according to the general procedure from 2-(2-iodophenyl)propionitrile[44b] (377 mg, 1.47 mmol). Yield 96% (362 mg, 1.41 mmol), dark orange oil. R_f=0.60 (25% EtOAc/hexane). IR (neat, cm^{-1}): 2980, 2241, 1601, 1349, 1145, 859, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.31 (dd, *J* = 7.2, 7.6 Hz, 1H), 4.90 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 6H), 1.34 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.1, 136.9, 132.0, 127.1, 126.6, 122.8, 84.0, 29.8, 24.9, 24.7, 22.6. LRMS (EI) *m/z* (relative intensity) 257 $[M]^+$ (37), 242 (13), 199 (73), 198 (40), 157 (100), 131 (36). HRMS (EI, $[M]^+$):calcd for $C_{15}H_{20}BNO_2$, 257.1587; found 257.1578.

2-(Benzyloxy)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (6C): Synthesis according to the general procedure from 2-(benzyloxy)-2-(2-iodophenyl)acetonitrile (221 mg, 0.632 mmol). Yield 49% (109 mg, 0.312 mmol), dark orange oil. R_f=0.59 (25% EtOAc/hexane). IR ν (neat, cm^{-1}): 2979, 1728, 1350, 1068, 698. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 7.8, 6.4 Hz, 1H), 7.42–7.31 (m, 6H), 6.15 (1H, s), 4.85 (d, *J* = 11.2 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H), 1.31 (s, 6H), 1.28 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.7, 136.5, 136.4, 131.8, 128.8, 128.5, 128.3, 128.2, 127.2, 118.3, 84.2, 72.1, 68.4, 24.9, 24.8. HRMS (FAB, $[M-CN]^+$): calcd for $C_{20}H_{24}BO_3$, 323.1819; found 323.1813.

Cyano(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl acetate (6D): Synthesis according to the general procedure from 2-(acetyloxy)-2-(2-iodophenyl)acetonitrile[14a] (246 mg, 0.817 mmol). Yield 67% (164 mg, 0.545 mmol), dark orange oil. R_f=0.51 (25% EtOAc/hexane). IR (neat, cm^{-1}): 2980, 1760, 1349, 1025, 658 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 6.4 Hz,

1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.45 (dd, *J* = 6.4, 7.2 Hz, 1H), 7.13 (s, 1H), 2.14 (s, 3H), 1.35 (s, 6H), 1.33 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.7, 137.4, 136.8, 131.9, 129.4, 127.7, 116.9, 84.4, 62.4, 24.84, 24.76, 20.5. LRMS (EI) *m/z* (relative intensity) 301 $[M]^+$ (12), 243 (50), 200 (38), 185 (46), 143 (100), 142 (34). HRMS (EI, $[M]^+$): calcd for $C_{16}H_{20}BNO_4$, 301.1485; found 301.1491.

2-(4,5-Dimethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (6E):

Synthesis according to the general procedure from 2-(2-iodo-4,5-dimethoxyphenyl)acetonitrile[44c] (606 mg, 2.00 mmol). The product was purified by silica gel chromatography eluting with 40% EtOAc/hexane. Yield 87% (527 mg, 1.74 mmol), white solid. R_f=0.31 (25% EtOAc/hexane). Mp: 132–135 °C. IR ν (compression cell, cm^{-1}): 2932, 2362, 1373, 1162, 668. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H), 6.94 (s, 1H), 4.09 (s, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 1.35 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.6, 147.9, 130.4, 119.2, 118.6, 111.8, 83.9, 56.0, 55.9, 24.9, 23.0. LRMS (EI) *m/z* (relative intensity) 303 $[M]^+$ (66), 302 (17), 245 (12), 203 (100), 202 (28), 177 (25). HRMS (EI, $[M]^+$): calcd for $C_{16}H_{22}BNO_4$, 303.1642; found 303.1653.

2-(4-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (6F):

Synthesis according to the general procedure from 2-(4-chloro-2-iodophenyl)acetonitrile[44d] (601 mg, 2.17 mmol). Yield 72% (437 mg, 1.57 mmol), grey solid. R_f=0.56 (25% EtOAc/hexane). Mp: 93–96 °C. IR ν (compression cell, cm^{-1}): 2981, 2245, 1486, 1343, 1141, 869. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 2.4 Hz, 1H), 7.43 (dd, *J* = 2.4, 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 4.05 (s, 2H), 1.36 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 136.5, 135.0, 133.7, 131.6, 130.0, 118.4, 84.5, 24.8, 23.0. LRMS (EI) *m/z* (relative intensity) 277 $[M]^+$ (76), 237 (32), 219 (88), 178 (46), 176 (100), 151 (44). HRMS (EI, $[M]^+$): calcd for $C_{14}H_{17}BClNO_2$, 277.1041; found 277.1046.

2-(5-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (6G):

Synthesis according to the general procedure from 2-(5-bromo-2-iodophenyl)acetonitrile (179 mg, 0.556 mmol). Yield 45% (80.1 mg, 0.249 mmol), brown oil. R_f=0.56 (25% EtOAc/hexane). IR ν (neat, cm^{-1}): 2989, 2245, 1586, 1347, 1150, 1059, 825. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 4.06 (s, 2H), 1.35 (s, 12H). ^{13}C-NMR (100

MHz, $CDCl_3$): δ 136.8, 136.6, 131.8, 128.5, 127.2, 118.9, 84.1, 24.9, 23.6. LRMS (EI) *m/z* (relative intensity) 323 $[M+2]^+$ (69), 321 $[M]^+$ (69), 280 (64), 265 (74), 263 (80), 223 (100), 221 (91). HRMS (EI, $[M]^+$): calcd for $C_{14}H_{17}O_2NBrB$, 321.0536; found 321.0521.

General procedure for the optimization of Pd(II)-catalyzed annulation of 1a with 6A (Table 1): To a test tube containing diphenylacetylene (**1a**, 0.10 mmol, 1 equiv), 2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetonitrile (**6A**, 0.12 mmol, 1.2 equiv), and catalysts ($Pd(OCOCF_3)_2$(dppe) (**11a**) for entries 1–7 and $[Pd(PhCN)_2(dppe)](BF_4)_2$ (**11b**) for entries 8 and 9, 5 or 2 μmol, 5 or 2 mol%) was added the solvent shown in Table 1 (0.5 mL). The resulting mixture was sealed with a screw cap, stirred under the reaction conditions shown in Table 1, cooled to room temperature, and then concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 2% EtOAc/toluene to yield 3,4-diphenyl-2-naphthylamine (**5a**) as a yellow solid.

entry 1: Yield 88% (27.0 mg, 91.4 μmol) from **1a** (18.6 mg, 104 μmol), **6A** (28.0 mg, 115 μmol), **11a** (3.7 mg, 5.1 μmol), and MeOH (0.5 mL).

entry 2: Yield 10% (3.1 mg, 10 μmol) from **1a** (18.6 mg, 104 μmol), **6A** (28.4 mg, 117 μmol), **11a** (4.0 mg, 5.5 μmol), and DMF (0.5 mL).

entry 3: Yield 6% (1.7 mg, 5.8 μmol) from **1a** (17.8 mg, 99.9 μmol), **6A** (29.4 mg, 121 μmol), **11a** (4.0 mg, 5.5 μmol), and acetone (0.5 mL).

entry 4: Yield 5% (1.4 mg, 4.7 μmol) from **1a** (18.6 mg, 104 μmol), **6A** (28.0 mg, 115 μmol), **11a** (3.9 mg, 5.3 μmol), and CH_3CN (0.5 mL).

entry 5: Yield <2% (<0.7 mg, 2 μmol) from **1a** (18.2 mg, 102 μmol), **6A** (28.4 mg, 117 μmol), **11a** (3.7 mg, 5.1 μmol), and 1,4-dioxane (0.5 mL).

entry 6: Yield 89% (26.9 mg, 91.1 μmol) from **1a** (18.3 mg, 103 μmol), **6A** (28.6 mg, 118 μmol), **11a** (3.6 mg, 4.9 μmol), and MeOH (0.5 mL).

entry 7: Yield 57% (17.8 mg, 60.3 μmol) from **1a** (18.9 mg, 106 μmol), **6A** (29.4 mg, 121 μmol), **11a** (1.5 mg, 2.1 μmol), and MeOH (0.5 mL).

entry 8: Yield 99% (29.2 mg, 98.9 μmol) from **1a** (17.8 mg, 99.9 μmol), **6A** (28.8 mg, 118 μmol), **11b** (4.5 mg, 5.1 μmol), and MeOH (0.5 mL).

entry 9: Yield 94% (28.5 mg, 96.5 μmol) from **1a** (18.2 mg, 102 μmol), **6A** (29.6 mg, 122 μmol), **11b** (1.9 mg, 2.1 μmol), and MeOH (0.5 mL).

3,4-Diphenylnaphthalen-2-amine (5a)[12a]: R_f=0.43 (2% EtOAc/toluene). Mp: 164–165 °C. IR ν (compression cell, cm^{-1}): 3466, 3373, 1619, 1344, 749. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.5 Hz, 1H), 7.38–7.34 (m, 2H), 7.24–7.09 (m, 13H), 3.47 (br–s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.2, 139.8, 139.1, 137.5, 134.4, 130.9, 130.6, 129.9, 128.3, 127.4, 127.3, 126.94, 126.91, 126.4, 126.1, 125.6, 122.5, 108.4. HRMS (ESI, $[M+H]^+$): calcd for $C_{22}H_{18}N$, 296.1434; found 296.1425.

General procedure for the Pd(II)-catalyzed annulation of 1b–q with 6A (Table 2): To a test tube containing internal alkyne **1b–q** (1 equiv), **6A** (1.2 equiv) and **11a** (5 mol%) was added anhydrous MeOH (0.2 M for **1**). The resulting mixture was sealed with a screw cap, stirred at 65 °C for 4 h, cooled to room temperature, and then concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 2% EtOAc/toluene, unless otherwise noted, to yield 3,4-disubstituted 2-naphthylamine **5b–q** and **5i–q′**.

3,4-Bis(4-methoxyphenyl)naphthalen-2-amine (5b)[14a] **(entry 1)**: Yield 70% (19.0 mg, 53.5 μmol) from **1b** (18.1 mg, 76.0 μmol), **6A** (22.2 mg, 91.1 μmol), and **11a** (2.8 mg, 3.8 μmol). White solid. R_f=0.27 (2% EtOAc/toluene). Mp: 184–185 °C. IR ν (compression cell, cm^{-1}): 3378, 2931, 2359, 1609, 1515, 1245, 1031, 751. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.35 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.12–7.09 (m, 2H), 7.05–7.00 (m, 4H), 6.79–6.75 (m, 4H), 3.78 (s, 3H), 3.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.3, 157.9, 142.7, 139.7, 134.3, 131.9, 131.65, 131.58, 129.8, 127.7, 127.0, 126.0, 125.5, 122.3, 113.8, 113.0, 108.0, 55.1. LRMS (EI) *m/z* (relative intensity) 355 $[M]^+$ (100), 324 (3), 280 (3), 252 (3), 239 (2), 177 (5). HRMS (EI, $[M]^+$): calcd for $C_{24}H_{21}NO_2$, 355.1572; found 355.1574.

3,4-Bis(4-acetylphenyl)naphthalen-2-amine (5c) (entry 2): Yield 74% (13.6 mg, 35.8 μmol) from **1c** (12.7 mg, 48.4 μmol), **6A** (14.0 mg, 58.1 μmol), and **11a** (1.8 mg, 2.4 μmol) through preparative TLC eluting with 33% EtOAc/toluene. Pale yellow solid. R_f=0.17 (10% EtOAc/toluene). Mp: 167–168 °C. IR ν (compression cell, cm^{-1}): 3473, 3369, 1684, 1606, 1267, 752. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84–7.69 (m, 4H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 7.0, 8.0 Hz, 1H), 7.28–

7.18 (m, 5H), 7.18 (s, 1H), 7.14 (dd, *J* = 8.3, 7.0 Hz, 1H), 3.71 (br–s, 2H), 2.57 (s, 3H), 2.56 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.8, 197.6, 144.1, 142.5, 141.7, 138.4, 135.8, 135.5, 134.6, 131.1, 130.9, 128.53, 128.47, 127.7, 126.7, 126.6, 126.4, 125.8, 122.9, 109.1, 26.5. HRMS (ESI, $[M+H]^+$): calcd for $C_{26}H_{22}NO_2$, 380.1645; found 380.1642.

3,4-Bis(2-methylphenyl)naphthalen-2-amine (5d) (entry 3): Yield 70% (22.6 mg, 69.9 μmol) from **1d** (20.5 mg, 99.4 μmol), **6A** (30.7 mg, 126 μmol), and **11a** (3.9 mg, 5.3 μmol). Pale yellow solid. R_f=0.43 (2% EtOAc/toluene). Mp: 183–188 °C. IR ν (compression cell, cm^{-1}): 3485, 3383, 3066, 3009, 2927, 1605, 1491, 1457, 1439, 1343, 1193, 841, 745. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 7.8, 6.8 Hz, 1H), 7.13–7.03 (m, 11H), 3.64 (br–s, 2H), 2.10 (s, 3H), 1.91 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.6, 139.0, 138.0, 136.8, 136.5, 136.1, 134.3, 132.04, 132.03, 130.0, 129.5, 129.4, 127.4, 127.1, 126.9, 126.7, 126.0, 125.6, 125.3, 124.5, 122.4, 107.8, 20.0, 19.3. LRMS (EI) *m/z* (relative intensity) 323 $[M]^+$ (100), 308 (11), 291 (3), 232 (5), 215 (3). HRMS (EI, $[M]^+$): calcd for $C_{24}H_{21}N$, 323.1674; found 323.1663.

3,4-Di(thiophen-3-yl)naphthalen-2-amine (5e) (entry 4): Yield 51% (15.3 mg, 49.8 μmol) from **1e** (18.6 mg, 97.8 μmol), **6A** (30.1 mg, 124 μmol), and **11a** (4.1 mg, 5.6 μmol) through preparative TLC eluting with 17% EtOAc/hexane. Pale yellow solid. R_f=0.36 (2% EtOAc/toluene). Mp: 130–136 °C. IR ν (compression cell, cm^{-1}): 3367, 3102, 1617, 1567, 1499, 1443, 1336, 1256, 1196, 838, 666. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.37 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.24 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.21 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.14 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.11 (s, 1H), 7.04 (dd, *J* = 2.9, 1.0 Hz, 1H), 6.96 (dd, *J* = 2.9, 1.0 Hz, 1H), 6.87 (dd, *J* = 4.9, 1.0 Hz, 1H), 6.85 (dd, *J* = 4.9, 1.0 Hz, 1H), 3.87 (br–s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.7, 139.1, 137.5, 135.5, 134.4, 130.2, 129.4, 127.4, 126.7, 126.3, 125.6, 125.4, 125.3, 124.3, 124.24, 124.19, 122.6, 108.4. LRMS (EI) *m/z* (relative intensity) 307 $[M]^+$ (100), 274 (21), 273 (22), 262 (7), 260 (5), 258 (7), 241 (5). HRMS (EI, $[M]^+$): calcd for $C_{18}H_{13}NS_2$, 307.0489; found 307.0475.

3,4-Dipropylnaphthalen-2-amine (5f) (entry 5): Yield 71% (28.0 mg, 123 μmol) from **1f** (19.1 mg, 173 μmol), **6A** (50.6 mg, 208 μmol), and **11a** (6.3 mg, 8.7 μmol). Brown oil. R_f=0.42 (2%

EtOAc/toluene). IR ν (neat, cm^{-1}): 3468, 3378, 2957, 1627, 1456, 1348, 742. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.31–7.21 (m, 2H), 6.90 (s, 1H), 3.78 (br–s, 2H), 3.01 (t, *J* = 8.3 Hz, 2H), 2.69 (t, *J* = 8.3 Hz, 2H), 1.70–1.59 (m, 4H), 1.12–1.06 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.9, 137.1, 133.7, 127.6, 127.0, 126.2, 125.0, 124.1, 122.3, 108.4, 31.0, 30.2, 24.4, 22.7, 14.75, 14.70. HRMS (ESI, $[M+H]^+$): calcd for $C_{16}H_{22}N$, 228.1747; found 228.1739.

7,8,9,10,11,12,13,14,15,16-Decahydrocyclododeca[*a*]naphthalen-6-amine (5g) (entry 6): Yield 51% (21.5 mg, 76.4 μmol) from **1g** (24.7 mg, 150 μmol), **6A** (43.8 mg, 180 μmol), and **11a** (5.5 mg, 7.5 μmol). Brown oil. R_f=0.40 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3471, 3380, 2926, 1625, 1443, 756. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.30 (dd, *J* = 8.1, 6.8 Hz, 1H), 7.23 (dd, *J* = 8.3, 6.8 Hz, 1H), 6.93 (s, 1H), 3.86 (br–s, 2H), 3.15 (t, *J* = 8.4 Hz, 2H), 2.84 (m, 2H), 1.80–1.51 (m, 16H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, 137.5, 133.7, 127.9, 127.4, 126.2, 125.0, 124.5, 122.3, 108.3, 28.9, 28.2, 28.1, 27.2, 27.0, 26.9, 26.8, 26.3, 22.3, 22.2. HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{28}N$, 282.2216; found 282.2212.

3,4-Bis((methoxymethoxy)methyl)naphthalen-2-amine (5h) (entry 7): Yield 50% (21.7 mg, 74.5 μmol) from **1h** (26.0 mg, 149 μmol), **6A** (43.6 mg, 179 μmol), and **11a** (5.5 mg, 7.5 μmol) through preparative TLC eluting with 40% EtOAc/toluene. Brown oil. R_f=0.11 (10% EtOAc/toluene). IR ν (neat, cm^{-1}): 3447, 3366, 2886, 1634, 1149, 1097, 1028. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.30 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.07 (s, 1H), 5.14 (s, 2H), 4.96 (s, 2H), 4.73 (s, 2H), 4.68 (s, 2H), 4.35 (br–s, 2H), 3.47 (s, 3H), 3.44 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.3, 135.0, 133.1, 127.2, 126.3, 126.2, 125.3, 124.5, 123.2, 111.3, 95.7, 95.0, 62.3, 61.8, 55.64, 55.60. LRMS (EI) *m/z* (relative intensity) 291 $[M]^+$ (100), 261 (11), 184 (40), 169 (41), 156 (27). HRMS (EI, $[M]^+$): calcd for $C_{16}H_{21}NO_4$, 291.1471; found 291.1466.

4-Methyl-3-phenylnaphthalen-2-amine (5i) and 3-methyl-4-phenylnaphthalen-2-amine (5i′) (entry 8): 4-Methyl-3-phenylnaphthalen-2-amine (**5i** as a faster-moving component; 38.5 mg, 73%) and 3-methyl-4-phenylnaphthalen-2-amine (**5i′** as a slower-moving component; 7.6 mg, 15%) were

obtained from **1i** (26.1 mg, 225 μmol), **6A** (58.9 mg, 242 μmol), and **11a** (7.3 mg, 10.0 μmol) through preparative TLC eluting with 20% EtOAc/hexane twice. **4-Methyl-3-phenylnaphthalen-2-amine (5i)**[12a]: Brown solid. R_f=0.43 (2% EtOAc/toluene). Mp: 95–99 °C. IR ν (compression cell, cm^{-1}): 3474, 3380, 3056, 2363, 1624, 760. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (dd,, *J* = 8.0, 1.2 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52–7.48 (m, 2H), 7.43–7.36 (m, 1H), 7.35–7.31 (m, 2H), 7.30–7.27 (m, 2H), 6.99 (s, 1H), 3.75 (br–s, 2H), 2.35 (3H, s). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.4, 138.5, 134.3, 132.8, 130.0, 129.0, 128.2, 127.5, 127.2, 126.1, 125.9, 124.5, 122.4, 106.8, 16.4. HRMS (ESI, $[M+H]^+$): calcd for $C_{17}H_{16}N$, 234.1277; found 234.1270. **3-Methyl-4-phenylnaphthalen-2-amine (5i′)**: Brown solid. R_f=0.36 (2% EtOAc/toluene). Mp: 121–125 °C. IR ν (compression cell, cm^{-1}): 3441, 3355, 3053, 1629, 1495, 1440, 1344, 748, 702, 620. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 1H), 7.48 (dd, *J* = 7.2, 7.7 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.30 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.09–7.06 (m, 2H), 3.83 (br–s, 2H), 2.05 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.2, 140.1, 139.6, 133.3, 130.2, 128.3, 127.8, 127.0, 126.5, 125.4, 125.3, 123.2, 122.3, 108.4, 15.2. HRMS (ESI, $[M+H]^+$): calcd for $C_{17}H_{16}N$, 234.1277; found 234.1273.

4-Isopropyl-3-phenylnaphthalen-2-amine (5j) and 3-isopropyl-4-phenylnaphthalen-2-amine (5j′) (entry 9): 3-Isopropyl-4-phenylnaphthalen-2-amine (**5j′** as a faster-moving component; 14.4 mg, 27%) and 4-isopropyl-3-phenylnaphthalen-2-amine (**5j** as a slower-moving component; 38.0 mg, 70%) were obtained from **1j** (29.9 mg, 207 μmol), **6A** (58.2 mg, 239 μmol), and **11a** (7.7 mg, 10.5 μmol). **4-Isopropyl-3-phenylnaphthalen-2-amine (5j)**: Brown solid. R_f=0.45 (2% EtOAc/toluene). Mp: 129–138 °C. IR ν (compression cell, cm^{-1}): 3488, 3391, 2960, 1622, 1440, 1336, 756, 709. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 7.9, 7.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.22 (dd, *J* = 8.1, 7.0 Hz, 1H), 6.96 (s, 1H), 3.49 (br–s, 2H), 3.23 (m, 1H), 1.43 (m, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 142.6, 142.3, 140.8, 139.2, 135.5, 129.2, 128.2, 127.4, 126.9, 125.4, 125.1, 122.3, 121.4, 110.9, 87.6, 22.3, 20.4. HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{20}N$, 262.1590; found 262.1583. **3-Isopropyl-4-phenylnaphthalen-2-amine (5j′)**: Brown solid. R_f=0.48 (2% EtOAc/toluene). Mp:

128–133 °C. IR ν (compression cell, cm^{-1}): 3495, 3382, 2973, 1618, 1565, 1489, 1437, 1339, 745, 698. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.29–7.24 (m, 3H), 7.04 (m, 3H), 3.99 (br–s, 1H), 3.18 (quint, *J* = 4.8 Hz, 1H), 1.30 (d, *J* = 4.8 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.6, 140.8, 139.3, 133.1, 132.2, 129.9, 128.2, 128.0, 127.0, 126.9, 125.4, 125.1, 122.3, 110.8, 30.2, 20.3. HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{20}N$, 262.1590; found 262.1584.

4-(*tert*-Butyl)-3-phenylnaphthalen-2-amine (5k) and 3-(*tert*-butyl)-4-phenylnaphthalen-2-amine (5k′) (entry 10): 3-(*tert*-Butyl)-4-phenylnaphthalen-2-amine (**5k′** as a faster-moving component; 6.4 mg, 12%) and 4-(*tert*-butyl)-3-phenylnaphthalen-2-amine (**5k** as a slower-moving component; 18.0 mg, 33%) were obtained from **1k** (31.5 mg, 199 μmol), **6A** (59.4 mg, 244 μmol), and **11a** (7.8 mg, 10.7 μmol). **4-(*tert*-Butyl)-3-phenylnaphthalen-2-amine (5k)**: Red solid. R_f=0.41 (2% EtOAc/toluene). Mp: 143–152 °C. IR ν (compression cell, cm^{-1}): 3504, 3391, 2960, 1621, 1331, 756, 705. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.43–7.36 (m, 3H), 7.33–7.27 (m, 3H), 7.22–7.19 (m, 1H), 6.96 (s, 1H), 3.40 (br–s, 2H), 1.39 (s, 9H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 144.1, 142.9, 141.2, 135.8, 130.8, 130.0, 128.7, 128.3, 127.2, 127.0, 126.9, 124.9, 120.5, 108.3, 38.6, 35.0. HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{22}N$, 276.1747; found 276.1744. **3-(*tert*-Butyl)-4-phenylnaphthalen-2-amine (5k′)**[14a]: All the analytical data were in good agreement with values reported in the literature.[14a]

2-(3-Amino-2-phenylnaphthalen-1-yl)propan-2-ol (5l) and 2-(3-amino-1-phenylnaphthalen-2-yl)propan-2-ol (5l′) (entry 11): 2-(3-Amino-2-phenylnaphthalen-1-yl)propan-2-ol (**5l** as a faster-moving component; 19.9 mg, 36%) and 2-(3-amino-1-phenylnaphthalen-2-yl)propan-2-ol (**5l′** as a slower-moving component; 18.0 mg, 33%) were obtained from **1l** (31.6 mg, 197 μmol), **6A** (59.6 mg, 245 μmol), and **11a** (8.0 mg, 10.9 μmol) through preparative TLC eluting with 12.5% EtOAc/toluene twice. **2-(3-Amino-2-phenylnaphthalen-1-yl)propan-2-ol (5l)**: Brown solid. R_f=0.37 (10% EtOAc/toluene). Mp: 187–193 °C. IR ν (compression cell, cm^{-1}): 3327, 2927, 2364, 1623, 1429, 705. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.60 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.46 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 7.9, 7.2 Hz, 1H), 7.26–7.22 (m,

3H), 7.01 (s, 1H), 3.45 (br–s, 2H), 1.63 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 142.7, 142.6, 140.7, 135.7, 129.7, 128.9, 128.6, 128.4, 127.4, 126.7, 125.7, 125.4, 121.5, 109.2, 76.1, 33.7. HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{19}NO$, 278.1539; found 278.1532. **2-(3-Amino-1-phenylnaphthalen-2-yl)propan-2-ol (5l′)**: Brown solid. R_f=0.26 (10% EtOAc/toluene). Mp: 166–173 °C. IR ν (compression cell, cm^{-1}): 3355, 2971, 1620, 1337, 1141, 756. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.40–7.38 (m, 3H), 7.28 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.20–7.19 (m, 2H), 7.04 (s, 1H), 6.99 (dd, *J* = 7.2, 8.6 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 4.21 (br–s, 2H), 1.34 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 144.6, 141.6, 137.6, 133.3, 132.0, 130.7, 128.4, 127.7, 127.4, 127.1, 126.0, 124.7, 122.1, 112.2, 76.6, 31.8. HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{19}NO$, 278.1539; found 278.1531.

3-Butyl-4-methylnaphthalen-2-amine (5m) and 4-butyl-3-methylnaphthalen-2-amine (5m′) (entry 12): 3-Butyl-4-methylnaphthalen-2-amine (**5m** as a faster-moving component; 18.2 mg, 40%) and 4-butyl-3-methylnaphthalen-2-amine (**5m′** as a slower-moving component; 15.0 mg, 33%) were obtained from **1m** (20.5 mg, 213 μmol), **6A** (58.0 mg, 238 μmol), and **11a** (7.0 mg, 9.6 μmol). **3-Butyl-4-methylnaphthalen-2-amine (5m):** Red oil. R_f=0.42 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3474, 3374, 2955, 1627, 1506, 1462, 1446, 742. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 8.1, 6.9 Hz, 1H), 7.24 (dd, *J* = 8.4, 6.9 Hz, 1H), 6.92 (s, 1H), 3.52 (br–s, 2H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.61 (s, 3H), 1.58–1.46 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 142.8, 133.3, 132.1, 128.2, 127.8, 126.1, 125.1, 124.1, 122.3, 108.1, 31.2, 28.0, 23.2, 14.7, 14.0. HRMS (ESI, $[M+H]^+$): calcd for $C_{15}H_{20}N$, 214.1590; found 214.1585. **4-Butyl-3-methylnaphthalen-2-amine (5m′):** Red oil. R_f=0.33 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3466, 3377, 2955, 1628, 1509, 1444, 742. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.30 (dd, *J* = 8.3, 6.7 Hz, 1H), 7.24 (dd, *J* = 8.3, 6.7 Hz, 1H), 6.93 (s, 1H), 3.78 (br–s, 2H), 3.07 (t, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 1.62–1.48 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.3, 137.2, 133.6, 126.9, 126.3, 124.9, 122.8, 122.3, 107.7, 32.5, 28.7, 213.2, 14.0, 13.5. HRMS (ESI, $[M+H]^+$): calcd for $C_{15}H_{20}N$, 214.1590; found 214.1586.

3-Isopropyl-4-methylnaphthalen-2-amine (5n) and 4-isopropyl-3-methylnaphthalen-2-amine (5n′) (entry 13): 3-Isopropyl-4-methylnaphthalen-2-amine (**5n** as a faster-moving component; 18.4 mg, 50%) and 4-isopropyl-3-methylnaphthalen-2-amine (**5n′** as a slower-moving component; 12.1 mg, 33%) were obtained from **1n** (15.2 mg, 185 μmol), **6A** (58.9 mg, 242 μmol), and **11a** (7.2 mg, 9.9 μmol). **3-Isopropyl-4-methylnaphthalen-2-amine (5n):** Brown oil. R_f=0.40 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3489, 3435, 2978, 1694, 1331, 731. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.30 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.24 (dd, *J* = 8.3, 7.2 Hz, 1H), 6.89 (1H, s), 3.85 (br–s, 2H), 3.72 (m, 1H), 2.66 (s, 3H), 1.45 (d, *J* = 7.2 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.4, 133.3, 132.8, 131.9, 128.2, 125.9, 125.2, 124.2, 122.4, 109.7, 28.2, 20.6, 15.5. HRMS (ESI, $[M+H]^+$): calcd for $C_{14}H_{18}N$, 200.1434; found 200.1430. **4-Isopropyl-3-methylnaphthalen-2-amine (5n′)**: Brown oil. R_f=0.32 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3479, 3373, 2927, 1626, 1445, 1239, 743. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.12 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.29 (dd, *J* = 7.2, 8.1 Hz, 1H), 7.21 (dd, *J* = 7.2, 7.6 Hz, 1H), 6.94 (s, 1H), 3.99 (m, 1H), 3.74 (br–s, 2H), 2.36 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.5, 142.3, 134.1, 126.7, 124.7, 123.0, 121.8, 108.4, 29.2, 21.9, 14.4. HRMS (ESI, $[M+H]^+$): calcd for $C_{14}H_{18}N$, 200.1434; found 200.1432.

3-(*tert*-Butyl)-4-methylnaphthalen-2-amine (5o) and 4-(*tert*-Butyl)-3-methylnaphthalen-2-amine (5o′) (entry 14): 3-(*tert*-Butyl)-4-methylnaphthalen-2-amine (**5o** as a faster-moving component; 8.5 mg, 22%) and 4-(*tert*-butyl)-3-methylnaphthalen-2-amine (**5o′** as a slower-moving component; 16.1 mg, 41%) were obtained from **1o** (17.8 mg, 185 μmol), **6A** (59.4 mg, 244 μmol), and **11a** (7.5 mg, 10.3 μmol). **3-(*tert*-Butyl)-4-methylnaphthalen-2-amine (5o)**[12a]: All the analytical data were in good agreement with values reported in the literature.[12a] **4-(*tert*-Butyl)-3-methylnaphthalen-2-amine (5o′)**: Red oil. R_f=0.32 (2% EtOAc/toluene). IR ν (neat, cm^{-1}): 3495, 3364, 2962, 1579, 1356, 754. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.23 (dd, *J* = 8.3, 8.1 Hz, 1H), 7.11 (dd, *J* = 8.8, 8.1 Hz, 1H), 6.88 (s, 1H), 3.74 (br–s, 2H), 2.44 (s, 3H), 1.71 (s, 9H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 145.7, 144.0, 134.3, 128.0, 127.0,

126.4, 124.8, 124.0, 120.1, 108.6, 38.8, 34.2, 18.4. HRMS (ESI, $[M+H]^+$): calcd for $C_{15}H_{20}N$, 214.1590; found 214.1590.

2-(3-Amino-1-methylnaphthalen-2-yl)propan-2-ol (5p) and 2-(3-amino-2-methylnaphthalen-1-yl)propan-2-ol (5p′) (entry 15): 2-(3-Amino-1-methylnaphthalen-2-yl)propan-2-ol (**5p** as a faster-moving component; 22.8 mg, 50%) and 2-(3-amino-2-methylnaphthalen-1-yl)propan-2-ol (**5p′** as a slower-moving component; 10.5 mg, 23%) were obtained from **1p** (20.5 mg, 209 μmol), **6A** (60.1 mg, 247 μmol), and **11a** (7.0 mg, 9.6 μmol) through preparative TLC eluting with 33% EtOAc/toluene twice and 50% EtOAc/hexane twice. **2-(3-Amino-1-methylnaphthalen-2-yl)propan-2-ol (5p)**: Brown solid. R_f=0.17 (10% EtOAc/toluene). Mp: 90–95 °C. IR ν (compression cell, cm^{-1}): 3374, 2974, 2361, 1623, 1366, 751. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 7.9, 7.2 Hz, 1H), 7.23 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.85 (s, 1H), 4.36 (br–s, 2H), 2.69 (s, 3H), 1.84 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.9, 134.2, 133.1, 131.6, 128.7, 125.7, 125.6, 124.2, 122.6, 111.6, 76.8, 31.3, 19.1. HRMS (ESI, $[M+H]^+$): calcd for $C_{14}H_{18}NO$, 216.1383; found 216.1380. **2-(3-Amino-2-methylnaphthalen-1-yl)propan-2-ol (5p′):** Brown solid. R_f=0.10 (10% EtOAc/toluene). Mp: 109–113 °C. IR ν (compression cell, cm^{-1}): 3406, 2360, 1623, 1456, 748. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.26 (dd, *J* = 8.1, 7.2 Hz, 1H), 7.15 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.93 (s, 1H), 3.77 (br–s, 2H), 2.46 (s, 3H), 1.93 (s, 6H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.92, 143.88, 134.3, 126.9, 126.35, 126.26, 124.5, 123.9, 121.0, 109.3, 76.2, 32.5, 17.6. HRMS (ESI, $[M+H]^+$): calcd for $C_{14}H_{18}NO$, 216.1383; found 216.1378.

4-(*tert*-Butyl)-3-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (5q) and 3-(*tert*-butyl)-4-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (5q′) (entry 16): 4-(*tert*-Butyl)-3-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (**5q** as a faster-moving component; 42.9 mg, 77%) and 4-(*tert*-butyl)-3-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (**5q′** as a slower-moving component; 1.7 mg, 3%) were obtained from **1q** (32.3 mg, 199 μmol), **6A** (61.0 mg, 251 μmol), and **11a** (7.7 mg, 10.5 μmol). **4-(*tert*-Butyl)-3-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (5q)**: Red solid. R_f=0.51 (2% EtOAc/toluene). Mp: 66–70 °C. IR ν (compression cell, cm^{-1}): 3481, 3382, 2967, 2360, 1622, 1262,

749. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.8 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.26 (dd, *J* = 7.7, 7.0 Hz, 1H), 7.13 (dd, *J* = 8.8, 7.0 Hz, 1H), 6.93 (1H, s), 4.56–4.36 (2H, br–s), 1.84 (9H, s), 1.38 (9H, s). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 148.2, 144.3, 135.5, 127.9, 127.0, 126.2, 125.3, 120.7, 110.6, 110.4, 107.3, 77.9, 38.9, 34.2, 30.6, 28.8. HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{26}N$, 280.2060; found 280.2056. **3-(*tert*-Butyl)-4-(3,3-dimethylbut-1-yn-1-yl)naphthalen-2-amine (5q′)**: All the analytical data were in good agreement with values reported in the literature.[14a]

General procedure for the Pd(II)-catalyzed annulation of 1a with 6B–G (Table 3): To a test tube containing internal alkyne **1a** (1 equiv), **6** (2 equiv for **6B–D**, 1.2 equiv for **6E–G**) and **11a** (5 mol%) was added anhydrous MeOH (0.2 M for **1a**). The resulting mixture was sealed with a screw cap, stirred at 65 °C for the time shown in Table 3, cooled to room temperature, and then concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 2% EtOAc/toluene, unless otherwise noted, to yield 3,4-diphenyl-2-naphthylamine **5B–G**.

1-Methyl-3,4-diphenylnaphthalen-2-amine (5B) (entry 1): Yield 81% (37.4 mg, 121 μmol) from **1a** (26.5 mg, 149 μmol), **6B** (76.6 mg, 298 μmol), and **11a** (5.4 mg, 7.4 μmol). Brown solid. R_f=0.49 (2% EtOAc/toluene). Mp: 179–180 °C. IR ν (compression cell, cm^{-1}): 3397, 3062, 1605, 1379, 1028, 752. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.9 Hz, 1H), 7.45 (dd, *J* = 8.9, 6.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.24–7.09 (m, 11H), 3.77 (br–s, 2H), 2.53 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 139.6, 139.5, 138.1, 137.7, 132.9, 131.0, 130.6, 129.8, 128.3, 127.6, 127.4, 126.9, 126.3, 126.0, 122.2, 122.0, 112.2, 12.2. HRMS (ESI, $[M+H]^+$): calcd for $C_{23}H_{20}N$, 310.1590; found 310.1578.

1-(Benzyloxy)-3,4-diphenylnaphthalen-2-amine (5C) (entry 2): Yield 91% (42.9 mg, 107 μmol) from **1a** (21.0 mg, 118 μmol), **6C** (82.1 mg, 236 μmol), and **11a** (4.3 mg, 5.9 μmol). Brown solid. R_f=0.62 (2% EtOAc/toluene). Mp: 150–151 °C. IR ν (compression cell, cm^{-1}): 3062, 2362, 2342, 1605, 1361, 757, 700. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47–7.43 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.25–7.11 (m, 12H), 5.12 (s, 2H), 3.88 (br–s, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 139.1, 137.8, 137.4, 135.7, 134.6, 131.2, 130.53, 130.45, 128.7, 128.3, 128.1, 127.9, 127.4, 127.3, 127.0, 126.4, 126.1, 122.5, 119.9, 74.0. LRMS (EI) *m/z*

(relative intensity) 401[M]$^+$ (4), 397 (2), 310 (100), 309 (5), 282 (5). HRMS (EI, [M]$^+$): calcd for $C_{29}H_{23}NO$, 401.1780; found 401.1760.

***N*-(1-Hydroxy-3,4-diphenylnaphthalen-2-yl)acetamide (5D′) (entry 3)**: Yield 92% (20.7 mg, 58.6 μmol) from **1a** (11.0 mg, 61.7 μmol), **6D** (37.2 mg, 124 μmol), and **11a** (2.3 mg, 3.1 μmol) through preparative TLC eluting with 10% EtOAc/toluene. Pale yellow solid. R_f=0.13 (2% EtOAc/toluene). Mp: 207–208 °C. IR ν (compression cell, cm^{-1}): 2362, 1646, 1494, 1399, 1273, 701, 617. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 9.56 (s, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 7.51 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.38 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.27–7.15 (m, 6H), 7.09–7.06 (m, 4H), 7.01 (br–s, 1H), 2.03 (s, 3H). ^{13}C-NMR (151

MHz, $CDCl_3$): δ 170.3, 144.3, 138.7, 136.8, 132.7, 131.9, 131.7, 131.3, 130.6, 128.5, 127.6, 126.9, 126.50, 126.46, 126.36, 125.6, 123.1, 117.9, 23.5. HRMS (EI, [M+H]$^+$): calcd for $C_{24}H_{20}NO_2$, 354.1489; found 354.1482.

6,7-Dimethoxy-3,4-diphenylnaphthalen-2-amine (5E)[14a] **(entry 4)**: Yield 81% (21.0 mg, 59.1 μmol) from **1a** (13.0 mg, 72.9 μmol), **6E** (26.5 mg, 87.5 μmol), and **11a** (2.7 mg, 3.6 μmol) through preparative TLC eluting with 10% EtOAc/toluene. Brown solid. R_f=0.13 (2% EtOAc/toluene). Mp: 170–171 °C. IR ν (compression cell, cm^{-1}): 2361, 2342, 1506, 702. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.21–7.19 (m, 4H), 7.15–7.11 (m, 6H), 7.05 (s, 1H), 6.98 (s, 1H), 6.70 (s, 1H), 3.99 (s, 3H), 3.66 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 149.9, 146.9, 141.1, 139.5, 138.5, 137.9, 130.77, 130.75, 130.2, 128.2, 128.0, 127.5, 126.7, 126.4, 122.3, 108.0, 106.2, 104.5, 55.8, 55.6. HRMS (ESI, [M+H]$^+$): calcd for $C_{24}H_{22}NO_2$, 356.1645; found 356.1635.

6-Chloro-3,4-diphenylnaphthalen-2-amine (5F) (entry 5): Yield 83% (27.2 mg, 82.5 μmol) from **1a** (17.7 mg, 99.3 μmol), **6F** (33.1 mg, 119 μmol), and **11a** (3.6 mg, 5.0 μmol). Brown solid. R_f=0.51 (2% EtOAc/toluene). Mp: 197–198 °C. IR ν (compression cell, cm^{-1}): 3369, 2361, 1616, 1487, 701, 619. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.35–7.07 (m, 13H), 3.73 (br–s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.7, 139.2, 138.4, 137.2, 132.7, 130.8, 130.4, 128.3, 127.9, 127.6, 127.12, 127.09, 126.9, 126.7, 125.7, 108.0. HRMS (ESI, [M+H]$^+$): calcd for $C_{22}H_{17}ClN$, 330.1044; found 330.1035.

7-Bromo-3,4-diphenylnaphthalen-2-amine (5G) (entry 6): Yield 78% (22.6 mg, 60.4 μmol) from **1a** (13.8 mg, 77.4 μmol), **6G** (22.6 mg, 92.9 μmol), and **11a** (2.8 mg, 3.9 μmol). Brown soild. R_f=0.46 (2% EtOAc/toluene). Mp: 158–160 °C. IR ν (compression cell, cm^{-1}): 3385, 3022, 2360, 1616, 1484, 1409, 933, 752, 700. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.24–7.06 (m, 12H), 7.01 (s, 1H), 3.82 (br–s, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 143.3, 140.0, 138.6, 137.1, 135.6, 130.8, 130.4, 128.8, 128.4, 127.5, 127.3, 127.1, 126.6, 125.7, 125.5, 120.5, 107.0. LRMS (EI) *m/z* (relative intensity) 375 $[M+2]^+$ (99), 373 $[M]^+$ (100), 295 (47), 293 (42), 276 (25), 217 (18). HRMS (EI, $[M]^+$): calcd for $C_{22}H_{16}BrN$, 373.0466; found 373.0450.

Preparation of *trans*-[Pd{C_6H_4(CH_2CN)-2}I(PPh_3)$_2$] (19a): A solution of $Pd(PPh_3)_4$ (1.16 g, 1.00 mmol) and 2-(2-iodophenyl)acetonitrile[44a] (365 mg, 1.50 mmol) in anhydrous benzene (28 mL) was stirred at room temperature for 96 h.[30] The reaction mixture was concentrated *in vacuo* and the title compound (841 mg, 0.962 mmol, 96%) was precipitated as a white solid from Et_2O. Mp: 217–220 °C (decomp). IR ν (compression cell, cm^{-1}): 3052, 2252, 1575, 1481, 1435, 1310, 1185, 1098, 1026, 739, 692. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.46–7.43 (m, 12H), 7.37–7.35 (m, 6H), 7.28–7.25 (m, 12H), 7.01–7.00 (m, 1H), 6.60 (t, J = 7.2 Hz, 1H), 6.46–6.44 (m, 2H), 3.23 (s, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 160.6 (s), 135.1 (t, J = 4.3 Hz), 134.7 (t, J = 5.8 Hz), 134.0 (s), 131.2 (t, J = 23 Hz), 130.2 (s), 128.6 (s), 128.0 (t, J = 4.3 Hz), 125.7 (s), 123.7 (s), 117.8 (s), 26.3 (s). ^{31}P-NMR (243 MHz, $CDCl_3$): δ 22.6 (s). HRMS (FAB, $[M-I]^+$): calcd for $C_{44}H_{36}NP_2Pd$, 746.1358; found 746.1358.

Synthesis of authentic [Pd{C_6H_4(CH_2CN)-2}(dppe)(PPh_3)](OCOCF_3) (20a): To a solution of **19a** (174 mg, 0.199 mmol) and dppe (79.8 mg, 0.200 mmol) in anhydrous CH_2Cl_2 (2 mL) was added Ag(OCOCF_3) (52.8 mg, 0.239 mmol) at room temperature. After being stirred at room temperature for 3 h, the reaction mixture was filtered through a Celite pad, which was thoroughly rinsed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the residue was suspended in acetone. Insoluble solid impurity was removed by the filtration and the filtrate was again evaporated under reduced pressure. The title compound (120 mg, 0.120 mmol, 60%) was precipitated as a white solid from EtOAc. Mp: 163–169 °C (decomp). IR ν (compression cell, cm^{-1}): 3055, 2255, 1691, 1435, 1200,

1156, 1114, 823, 740, 694. ^{1}H-NMR (600 MHz, acetone-d_6): δ 7.90–7.85 (m, 4H), 7.75–7.64 (m, 6H), 7.50 (t, J = 6.9 Hz, 1H), 7.42 (t, J = 6.7 Hz, 3H), 7.36 (t, J = 6.9 Hz, 1H), 7.26–7.19 (m, 10H), 7.10–7.07 (m, 7H), 6.91–6.86 (m, 5H), 6.70 (d, J = 5.4 Hz, 1H), 6.59 (t, J = 6.7 Hz, 1H), 3.04 (d, J = 12.4 Hz, 1H), 2.81 (d, J = 12.4 Hz, 1H), 2.93–2.67 (m, 3H), 2.53–2.49 (m, 1H). ^{31}P-NMR (243 MHz, acetone-d_6): δ 46.0 (dd, J = 26, 355 Hz), 38.2 (dd, J = 26, 26 Hz), 17.5 (dd, J = 26, 355 Hz). ^{19}F-NMR (565 MHz, acetone-d_6): δ –73.7. HRMS (FAB, $[M\text{-}TFA]^+$): calcd for $C_{52}H_{45}NP_3Pd$, 882.1794; found 882.1815.

Synthesis of [Pd{$C_6H_4(CH_2CN)$-2}(dppe)(PPh_3)](OCOCF_3) (20a) via transmetalation between 11a and 6A: To a NMR tube containing **11a** (10 μmol, 1 equiv.), **6A** (11 μmol, 1.1 equiv.), and triphenylphosphine (11 μmol, 1.1 equiv) was added a solvent (methanol-d_4, acetone-d_6, acetonitrile-d_3, or chloroform-d, 1.0 mL). The resulting mixture was sealed with a cap and heated at 65 °C for 24 h. ^{1}H and ^{31}P NMR spectra of the mixture only in methanol-d_4 were identical with those of the authentic sample obtained by the above procedure.

methanol-d_4: **11a** (7.3 mg, 10 μmol), **6A** (2.8 mg, 12 μmol), and PPh_3 (3.0 mg, 11 μmol).

acetone-d_6: **11a** (7.4 mg, 10 μmol), **6A** (2.7 mg, 11 μmol), and PPh_3 (3.0 mg, 11 μmol).

acetonitrile-d_3: **11a** (7.3 mg, 10 μmol), **6A** (2.7 mg, 11 μmol), and PPh_3 (3.0 mg, 11 μmol).

chloroform-d: **11a** (7.2 mg, 9.9 μmol), **6A** (2.8 mg, 12 μmol), and PPh_3 (2.9 mg, 11 μmol).

General procedure for the stoichiometric annulation of 1a with 20a (Scheme 5): To a test tube containing **20a** (10 μmol) and **1a** (20 μmol) was added anhydrous solvent (0.2 mL). The resulting mixture was sealed with a screw cap, stirred at 65 °C for 4 h, cooled to room temperature, and then concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 2% EtOAc/toluene to yield **5a**.

methanol: Yield 48% (1.4 mg, 4.7 μmol) from **20a** (9.9 mg, 9.9 μmol) and **1a** (3.8 mg, 21 μmol).

acetonitrile: Yield 42% (1.3 mg, 4.4 μmol) from **20a** (10.4 mg, 10 μmol) and **1a** (3.6 mg, 20 μmol).

acetone: Yield 37% (1.1 mg, 3.7 μmol) from **20a** (9.9 mg, 9.9 μmol) and **1a** (3.7 mg, 21 μmol).

1,4-dioxane: Yield 29% (0.9 mg, 3.0 μmol) from **20a** (10.3 mg, 10 μmol) and **1a** (3.7 mg, 21 μmol).

Synthesis of authentic [Pd{C_6H_4(CN)-2}(dppe)(PPh_3)](OCOCF_3) (20b) (Scheme 5): To a solution of **19b** (203 mg, 250 mmol) and dppe (100 mg, 251 μmol) in anhydrous CH_2Cl_2 (5 mL) was added Ag(OCOCF_3) (66.4 mg, 301 mmol) at room temperature. After being stirred at room temperature for 6 h, the reaction mixture was filtered through a Celite pad, which was thoroughly rinsed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the residue was suspended in EtOH. Insoluble solid impurity was removed by the filtration. The filtrate was again evaporated under reduced pressure and the residue was precipitated from EtOAc to give the title compound (169 mg, 172 μmol, 69%) as a white solid. Mp: 194–198 °C (decomp). IR ν (compression cell, cm^{-1}): 3569, 3407, 3059, 2217, 1684, 1482, 1436, 1198, 1163, 1117, 744, 694. ^{1}H-NMR (600 MHz, acetone-d_6): δ 8.12–8.09 (m, 2H), 7.98–7.94 (m, 2H), 7.82–7.77 (m, 2H), 7.74 (t, J = 7.2 Hz, 2H), 7.67 (t, J = 7.8 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.44–7.40 (m, 3H), 7.30 (t, J = 7.8 Hz, 1H), 7.28–7.26 (m, 2H), 7.23–7.20 (m, 12H), 7.18–7.16 (m, 2H), 7.13 (d, J = 6.6 Hz, 1H), 7.00–6.97 (m, 2H), 6.90 (dd, J = 6.6, 7.8 Hz, 1H), 6.81–6.78 (m, 2H), 6.76 (dd, J = 7.8, 7.2 Hz, 1H), 6.67 (d, J = 7.2 Hz, 1H), 2.90–2.60 (m, 3H), 2.44–2.36 (m, 1H). ^{31}P-NMR (243 MHz, acetone-d_6): δ 49.7 (dd, J = 26, 355 Hz), 42.1 (dd, J = 26, 26 Hz), 19.4 (dd, J = 26, 355 Hz). ^{19}F-NMR (565 MHz, acetone-d_6): δ –73.7. HRMS (FAB, $[M\text{-}TFA]^+$): calcd for $C_{51}H_{43}NP_3Pd$, 868.1638; found 868.1661.

Synthesis of [Pd{C_6H_4(CN)-2}(dppe)(PPh_3)](OCOCF_3) (20b) via transmetalation between 11a and 12 (Scheme 5): To a NMR tube containing **11a** (7.3 mg, 10 μmol), **12** (1.6 mg, 11 μmol), and PPh_3 (2.9 mg, 11 μmol) was added methanol-d_4 (1.0 mL). The resulting mixture was sealed with a cap and heated at 65 °C for 24 h. ^{1}H and ^{31}P NMR spectra of the mixture were identical with those of the authentic sample obtained by the above procedure.

General procedure for the stoichiometric annulation of 1a with 20b (Scheme 5): To a test tube containing **20b** (10 μmol) and **1a** (20 μmol) was added anhydrous solvent (0.2 mL). The resulting mixture was sealed with a screw cap, stirred at 80 °C for 24 h, cooled to room temperature, and then

concentrated *in vacuo*. The residue was purified by preparative TLC eluting with 1% EtOAc/toluene to yield **9**.

methanol: Yield 17% (0.5 mg, 1.8 μmol) from **20b** (9.8 mg, 10 μmol) and **1a** (3.6 mg, 20 μmol).

acetonitrile: Yield 31% (0.9 mg, 3.2 μmol) from **20b** (9.9 mg, 10 μmol) and **1a** (3.6 mg, 20 μmol).

acetone: Yield 63% (1.8 mg, 6.4 μmol) from **20b** (9.8 mg, 10 μmol) and **1a** (3.7 mg, 21 μmol).

1,4-dioxane: Yield 40% (1.2 mg, 4.3 μmol) from **20b** (10.2 mg, 11 μmol) and **1a** (3.8 mg, 21 μmol).

Preparation of [Pd{$C_6H_4(CH_2CN)$-2}I(dppe)] (23a): To a test tube containing Pd(η^3-C_3H_5)(η^3-C_5H_5)[47] (42.2 mg, 199 μmol), dppe (88.1 mg, 221 μmol), and 2-(2-iodophenyl)acetonitrile[44a] (116.5 mg, 479 μmol) was added anhydrous 1,4-dioxane (2 mL). The resulting mixture was sealed with a screw cap, stirred at 65 °C for 12 h, cooled to room temperature, and then filtered through a Celite pad, which was thoroughly rinsed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the title compound (94.5 mg, 126 μmol, 64%) was precipitated as a yellow solid from EtOAc. Mp: 226–233 °C (decomp). IR ν (compression cell, cm^{-1}): 3056, 2253, 1573, 1483, 1434, 1188, 1104, 1026, 821, 744, 692. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 6.9, 8.6 Hz, 1H), 7.80–7.72 (m, 2H), 7.55–7.45 (m, 10H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.3, 8.2 Hz, 1H), 7.16 (dt, *J* = 5.5, 7.6 Hz, 1H), 6.98 (d, *J* = 4.1 Hz, 1H), 6.81–6.76 (m, 4H), 3.77 (d, *J* = 18.6 Hz, 1H), 3.30 (d, *J* = 18.6 Hz, 1H), 2.71–2.58 (m, 1H), 2.53–2.46 (m, 1H), 2.41–2.28 (m, 1H), 1.90–1.82 (m, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 155.4 (d, *J* = 133 Hz), 136.9 (d, *J* = 4.5 Hz), 135.3 (s), 134.4 (d, *J* = 12 Hz), 134.0 (d, *J* = 13 Hz), 133.2 (d, *J* = 11 Hz), 132.0 (s), 131.3 (s), 131.3 (d, *J* = 8.8 Hz), 131.2 (d, *J* = 36 Hz), 131.0 (s), 130.8 (s), 130.3 (d, *J* = 35 Hz), 129.7 (d, *J* = 48 Hz), 129.2 (d, *J* = 13 Hz), 129.1 (d, *J* = 10 Hz), 128.7 (d, *J* = 10 Hz), 128.5 (d, *J* = 10 Hz), 128.2 (d, *J* = 51 Hz), 128.1 (d, *J* = 7.4 Hz), 125.5 (d, *J* = 8.6 Hz), 123.7 (s), 118.7 (s), 29.1 (dd, *J* = 21, 30 Hz), 28.3 (s), 24.4 (dd, *J* = 13, 26 Hz). ^{31}P-NMR (243 MHz, $CDCl_3$): δ 48.1 (d, *J* = 26 Hz), 35.3 (d, *J* = 26 Hz). HRMS (FAB, [M-I]$^+$): calcd for $C_{34}H_{30}NP_2Pd$, 620.0888; found 620.0900.

Pd(II)-catalyzed annulation of 1a with 6E under catalysis of 23a and Ag($OCOCF_3$) in methanol (Scheme 6): To a test tube containing **6E** (30.2 mg, 99.6 μmol), **1a** (21.7 mg, 122 μmol), **23a** (7.6 mg, 10 μmol)**,** and Ag($OCOCF_3$) (2.4 mg, 11 μmol) was added anhydrous methanol (0.5 mL). The resulting mixture was sealed with a screw cap, stirred at 65 °C for 2 h, cooled to room temperature, and then filtered through a Celite pad, which was thoroughly rinsed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the residue was separated by preparative TLC eluting with 25% EtOAc/hexane twice to give impure **5a** (3.1 mg) and **5E** (30.0 mg). Faster-moving **5a** was further purified by NH_2 silica gel 60 F_{254} plate eluting with 17% EtOAc/hexane twice to yield **5a** (2.2 mg, 7.4 μmol, 73% based on **23a**). Slower-moving **5E** was further purified by NH_2 silica gel 60 F_{254} plate eluting with 25% EtOAc/hexane five times to yield **5E** (26.8 mg, 75.4 μmol, 76% based on **6E**).

Pd(II)-catalyzed annulation of 1a with 6E under catalysis of 23a and Ag($OCOCF_3$) in acetonitrile (Scheme 6): To a test tube containing **6E** (30.1 mg, 99.3 μmol), **1a** (22.6 mg, 127 μmol), **23a** (7.6 mg, 10 μmol)**,** and Ag($OCOCF_3$) (2.5 mg, 11 μmol) was added anhydrous acetonitrile (0.5 mL). The resulting mixture was sealed with a screw cap, stirred at 65 °C for 27 h, cooled to room temperature, and then filtered through a Celite pad, which was thoroughly rinsed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the residue was separated by preparative TLC eluting with 25% EtOAc/hexane twice to give **5a** (2.5 mg, 8.5 μmol, 83% based on **23a**) and **6E** (16.2 mg, 53.4 μmol, 54% recovery) along with impure **5E** (4.1 mg), which was further purified by NH_2 silica gel 60 F_{254} plate eluting with 25% EtOAc/hexane five times to yield **5E** (2.2 mg, 6.2 μmol, 6% based on **6E**).

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting Information.

Copies of ^{1}H and ^{13}C NMR spectra for synthetic compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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