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1-Bromo-2-(cyclopropylidenemethyl)benzene: A Useful Building Block in the Palladium-Catalyzed Reaction of 2-Alkynylbenzenamine

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Abstract: A novel palladium-catalyzed domino reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylbenzenamine is reported, which generates 2-(naphthalen-2-yl)benzenamines and 5*H*-indeno[1,2-*c*]quinolines via 6-*endo* and 5-*exo* cyclization, respectively. The regioselectivity for the final outcome can be affected by phosphine and N-heterocyclic carbene ligands.

Keywords: cyclization · domino reactions · homogeneous catalysis · palladium · synthetic methods

Introduction

Domino processes, in which one reagent or catalyst promotes sequential reactions in a defined order, have been widely used in organic synthesis.[1,2] Currently, this approach is attractive for the generation of molecular diversity and complexity in the field of chemical genetics.[3] As part of a continuing effort in our laboratory for accessing privileged scaffolds, we have been interested in the development of cascade strategies for the construction of natural-product-like compounds.[4,5] Recently, we disclosed a novel transformation for access to indene-incorporating molecules via a palladium-catalyzed reaction of 2-alkynylhalobenzene with related compounds.[5] The reaction process involved a double insertion of triple bonds. This synthetic sequence is highly selective and generates complex molecules with high efficiency. Inspired by this study, we conceived that 1-bromo-2-(cyclopropylidenemethyl)benzene would be an interesting building block as well, due to its versatility in organic synthesis.[6] We now report an example by combination of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylbenzenamine in the presence of a palladium catalyst, leading to an efficient preparation of 2-(naphthalen-2-yl)-benzenamines and 5*H*-indeno[1,2-*c*]quinolines.

Due to the structural similarity of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylhalobenzene, we envisioned that the transformation of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylbenzenamine was possible. As described in Scheme 1, an oxidative addition of palladium(0) to 1-bromo-2-(cyclopropylidenemethyl)benzene **1** would occur first to generate a palladium(II) species **A**. Then 2-alkynylbenzenamine **2** would be involved via coordination of the triple bond with Pd^{II}. After insertion of Pd^{II} into the triple bond, an intermediate **B** would be afforded. The subsequent intramolecular insertion of Pd^{II} to the double bond would result in two possible pathways (6-*endo* and 5-*exo*). If the conversion proceeds along path I via 5-*exo* cyclization, species **C** would be formed, which then proceeds through C–N coupling[7] to furnish compound **D**. After intramolecular rearrangement, product **4** would be obtained. In the meantime, another pathway (path II) could not be excluded. After 6-*endo* cyclization, the intermediate **F** would be generated. This species could easily undergo rearrangement and β-H elimination to afford 2-(naphthalen-2-yl)benzenamine **3**. The hypothesis in Scheme 1 seems feasible. Moreover, during the transformation, molecular complexity and diversity could be ensured. Therefore, we started to explore the possibility of this conversion.

Results and Discussion

On the basis of the chemistry presented in Scheme 1, our first attempt was performed for the reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene **1a** with 2-alkynylbenzenamine **2a** (Table 1). At the outset, the reaction was catalyzed by $[Pd_2(dba)_3]$ in the presence of *t*BuONa in 1,4-dioxane under reflux conditions (Table 1, entry 1). However, the reaction was not promising, and no reaction occurred. No improvement was observed by addition of PCy_3 as the ligand (Table 1, entry 2). A trace amount of product was detected when palladium chloride or palladium bromide was

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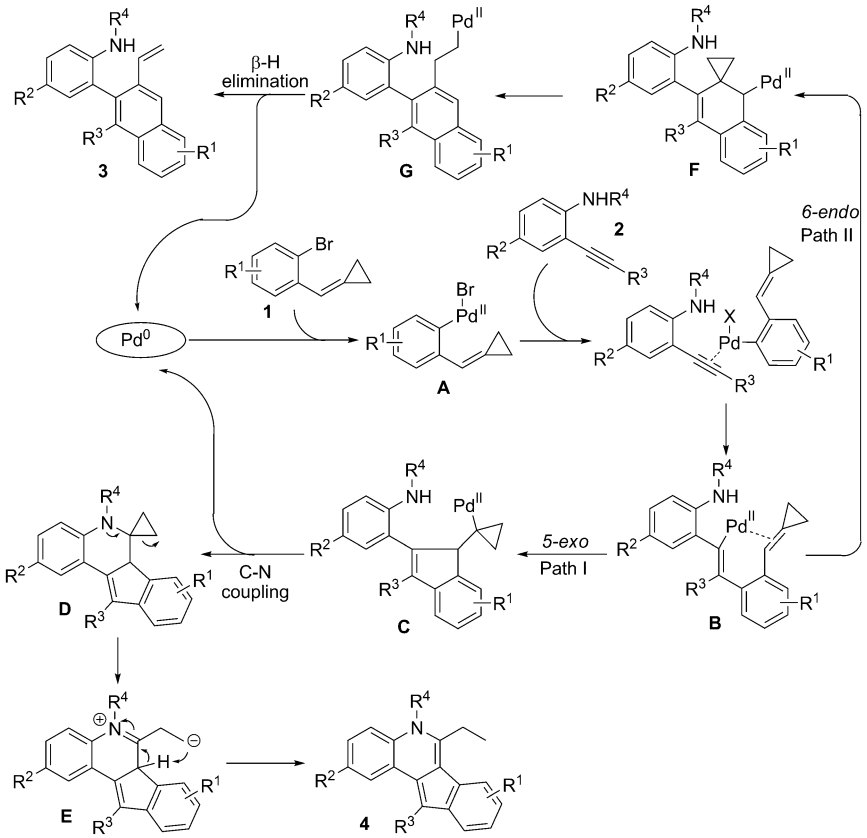
Supporting information for this article, including experimental procedure, characterization data, ^1H and ^{13}C NMR spectra of compounds **3** and **4**, and X-ray crystal data of compound **3a** and **4a**, is available on the WWW under http://dx.doi.org/10.1002/asia.201200122.



Scheme 1. A possible mechanism for the palladium-catalyzed reaction of 1-bromo-2-(cyclopropylidenemethyl)-benzene and 2-alkynylbenzenamine.

used as catalyst in the reaction (Table 1, entries 3 and 4). To our delight, the expected products were generated when palladium acetate was utilized (Table 1, entry 5). Interestingly, the products via 6-*endo* and 5-*exo* cyclization were both observed and isolated (**3a**, 25% yield; **4a**, 20% yield). A similar outcome was obtained when $Pd(CO_2CF_3)_2$ was employed in the conversion (Table 1, entry 6). Further investigation revealed that the selectivity could be improved by changing the catalyst to $[Pd(PhCN)_2Cl_2]$ or $[Pd(PPh_3)_2Cl_2]$ (Table 1, entries 7 and 8). However, the result was inferior when the reaction temperature was reduced to 85°C (Table 1, entry 9). We next screened other bases and solvents; however, no better results were obtained (Table 1, entries 10–19). Thus, we shifted our focus to the ligands. Different phosphine ligands such as PPh_3, $P(C_6F_5)_3$, P*t*Bu$_3$, X-Phos, dppf, and others developed by Buchwald[7f] were examined (Table 1, entries 20–30). Gratifyingly, a good result was obtained when L4 was utilized as a ligand in the reaction (Table 1, entry 28: **3a**, 31% yield; **4a**, 64% yield). Further screening of N-heterocyclic carbene ligands disclosed that NHC L7 gave rise to an interesting outcome, which generated product **3a** in 71% yield and compound **4a** in 20% yield, respectively (Table 1, entry 31). From these results, it seems that the yield and selectivity are complementary by using L4 or L7 as the ligand in the reaction.

Next, investigations with various 1-bromo-2-(cyclopropylidenemethyl)benzenes **1** and 2-alkynylbenzenamines **2** were conducted under the optimized conditions (5 mol% $[Pd(PPh_3)_2Cl_2]$, 10 mol% phosphine L4 or NHC L7, *t*BuONa, 1,4-dioxane, 105°C). Table 2 summarizes results for the evaluation of the palladium-catalyzed reactions. For the reactions of 1-bromo-2-(cyclopropylidenemethyl)benzene **1a**, 2-alkynylbenzenamines with aryl or heteroaryl groups attached on the triple bond were all suitable substrates under the standard conditions. For instance, 1-bromo-2-(cyclopropylidenemethyl)benzene **1a** reacted with 2-alkynylbenzenamine **2e** (a 2-thiophenyl group attached on the triple bond) in the presence of a phosphine ligand L4, giving rise to compounds **3e** and **4e** in 27% and 71% yield, respectively (Table 2, entry 5). The selectivity was reversed when NHC L7 was employed in the reaction, which afforded the desired products **3e** and **4e** in 74% and 23% yield, respectively (Table 2, entry 5). However, the conditions were not suitable for 2-alkynylbenzenamines with an alkyl group attached to the triple bond. Only a trace amount of product was detected when R^3 was changed to a cyclopropyl group. A similar outcome was observed when R^3 was *n*-butyl group in the above reaction (data not shown in Table 2). For the reactions of 1-bromo-2-(cyclopropylidenemethyl)benzene **1a**, 2-alkynylbenzenamines **2** with different substitutions on the aromatic ring were examined subsequently (Table 2, entries 6–10). Methyl, isopropyl, chloro, and trifluoromethyl groups were all tolerated under the standard conditions. 2-Alkynylbenzenamines **2** with substitution on the amino groups were tested in the meantime. It was found that *N*-benzyl-2-alkynylbenzenamine **2k** was effective in the conversion (Table 2, entry 11). However, the reaction did not proceed when R^4 was changed to an acetyl group (Table 2, entry 12). Subsequently, reactions of 2-alkynylbenzenamine **2a** with substituted 1-bromo-2-(cyclopropylidenemethyl)-benzenes were explored (Table 2, entries 13–16). As we can see, all reactions proceeded well to afford the corresponding products in good yields.

Conclusions

We have described a novel and efficient pathway for the generation of 2-(naphthalen-2-yl)benzenamines and 5*H*-

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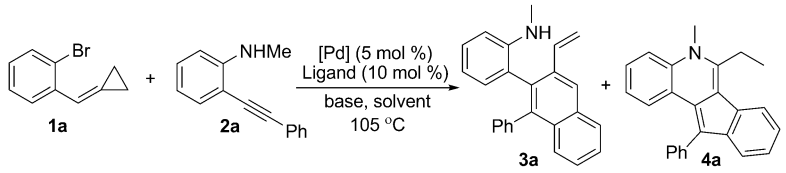
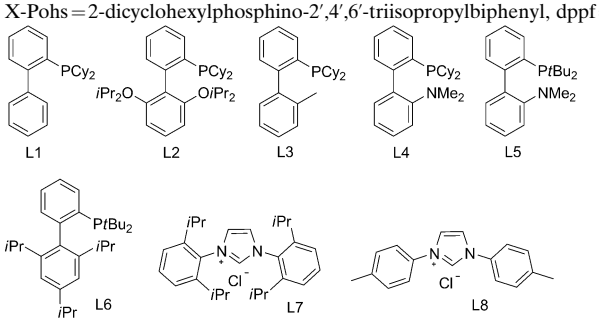
Table 1. Initial studies for the palladium-catalyzed reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene **1a** with 2-alkynylbenzenamine **2a**.



Entry	[Pd]	Ligand	Base	Solvent	T [°C]	Yield [%][a]	
						3a	**4a**
1	$[Pd_2(dba)_3]$	none	*t*BuONa	1,4-dioxane	105	/	
2	$[Pd_2(dba)_3]$	PCy_3	*t*BuONa	1,4-dioxane	105	/	
3	$PdCl_2$	PCy_3	*t*BuONa	1,4-dioxane	105	trace	
4	$PdBr_2$	PCy_3	*t*BuONa	1,4-dioxane	105	trace	
5	$Pd(OAc)_2$	PCy_3	*t*BuONa	1,4-dioxane	105	25	20
6	$Pd(CO_2CF_3)_2$	PCy_3	*t*BuONa	1,4-dioxane	105	30	23
7	$[Pd(PhCN)_2Cl_2]$	PCy_3	*t*BuONa	1,4-dioxane	105	40	25
8	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuONa	1,4-dioxane	105	44	30
9	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuONa	1,4-dioxane	85	15	18
10	$[Pd(PPh_3)_2Cl_2]$	PCy_3	K_2CO_3	1,4-dioxane	105	/	
11	$[Pd(PPh_3)_2Cl_2]$	PCy_3	K_3PO_4	1,4-dioxane	105	/	
12	$[Pd(PPh_3)_2Cl_2]$	PCy_3	Cs_2CO_3	1,4-dioxane	105	/	
13	$[Pd(PPh_3)_2Cl_2]$	PCy_3	KOH	1,4-dioxane	105	30	23
14	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuOLi	1,4-dioxane	105	/	
15	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuOK	1,4-dioxane	105	24	20
16	$[Pd(PPh_3)_2Cl_2]$	PCy_3	NaOMe	1,4-dioxane	105	/	
17	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuONa	toluene	105	trace	
18	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuONa	DMF	105	/	
19	$[Pd(PPh_3)_2Cl_2]$	PCy_3	*t*BuONa	DMSO	105	/	
20	$[Pd(PPh_3)_2Cl_2]$	PPh_3	*t*BuONa	1,4-dioxane	105	23	20
21	$[Pd(PPh_3)_2Cl_2]$	$P(C_6F_5)_3$	*t*BuONa	1,4-dioxane	105	/	
22	$[Pd(PPh_3)_2Cl_2]$	$PtBu_3{\cdot}HBF_4$	*t*BuONa	1,4-dioxane	105	/	
23	$[Pd(PPh_3)_2Cl_2]$	X-Phos	*t*BuONa	1,4-dioxane	105	37	28
24	$[Pd(PPh_3)_2Cl_2]$	dppf	*t*BuONa	1,4-dioxane	105	12	15
25	$[Pd(PPh_3)_2Cl_2]$	L1	*t*BuONa	1,4-dioxane	105	33	27
26	$[Pd(PPh_3)_2Cl_2]$	L2	*t*BuONa	1,4-dioxane	105	31	46
27	$[Pd(PPh_3)_2Cl_2]$	L3	*t*BuONa	1,4-dioxane	105	36	28
28	$[Pd(PPh_3)_2Cl_2]$	L4	*t*BuONa	1,4-dioxane	105	31	64
29	$[Pd(PPh_3)_2Cl_2]$	L5	*t*BuONa	1,4-dioxane	105	35	46
30	$[Pd(PPh_3)_2Cl_2]$	L6	*t*BuONa	1,4-dioxane	105	45	20
31	$[Pd(PPh_3)_2Cl_2]$	L7	*t*BuONa	1,4-dioxane	105	71	20
32	$[Pd(PPh_3)_2Cl_2]$	L8	*t*BuONa	1,4-dioxane	105	23	40

[a] Yield of isolated product based on 2-alkynylbenzenamine **2a**. dba = dibenzylideneacetone, Cy = cyclohexyl, X-Pohs = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, dppf = 1,1′-bis(diphenylphosphino)ferrocene.



indeno[1,2-*c*]quinolines via a palladium-catalyzed domino reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylbenzenamine. The regioselectivity of 6-*endo* and 5-*exo* cyclization for the final outcome depends on the ligand utilized in the reaction. Phosphine L4 and NHC L7 are found to be complementary for the regioselectivity in the reaction. Exploration of 1-bromo-2-(cyclopropylidenemethyl)benzenes for other transformations is under investigation currently.

Experimental Section

General experimental procedure for the palladium-catalyzed reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene with 2-alkynylbenzenamine

A solution of 1-bromo-2-(cyclopropylidenemethyl)benzene **1** (0.6 mmol) in 1,4-dioxane (2.0 mL) was added to a mixture of 2-alkynylbenzenamine **2** (0.3 mmol), $[Pd(PPh_3)_2Cl_2]$ (10.5 mg, 0.015 mmol), ligand (0.03 mmol), and *t*BuONa (72.0 mg, 0.75 mmol). The reaction was stirred under reflux. After completion of reaction as indicated by TLC, the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a thin layer of silica gel, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (eluted with petroleum ether/ethyl acetate = 30:1 to 8:1) to provide the products **3** and **4**.

*N-Methyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)aniline (**3a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 3H), 3.32 (s, 1H), 5.17 (dd, J = 11.2, 1.2 Hz, 1H), 5.80 (dd, J = 17.6, 1.2 Hz, 1H), 6.46–6.57 (m, 3H), 6.76 (dd, J = 7.2, 1.2 Hz, 1H), 7.07–7.09 (m, 2H), 7.14–7.26 (m, 4H), 7.32–7.34 (m, 1H), 7.45–7.51 (m, 2H), 7.91 (d, J = 8.4 Hz, 1H), 8.16 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 109.6, 115.5, 116.4, 124.2, 125.0, 126.1, 126.3, 126.9, 126.9, 127.4, 127.6, 128.2, 128.4, 129.2, 131.0, 131.1, 133.3, 134.8, 135.6, 135.8, 135.8, 138.8, 140.3, 146.9 ppm; HRMS (ESI) calcd for $C_{25}H_{21}N$: 336.1752 (M+H$^+$), found: 336.1755.

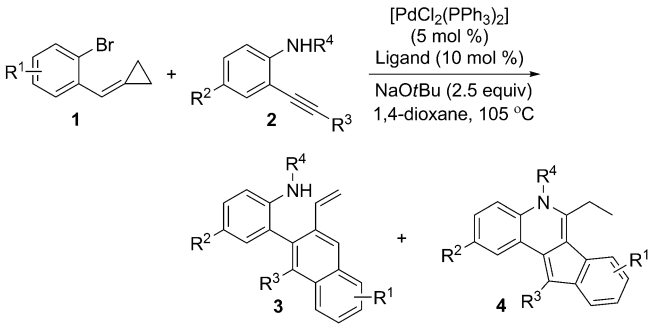
*6-Ethyl-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4a**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (t, J = 7.6 Hz, 3H), 3.39 (q, J = 7.6 Hz, 2H), 3.71 (s, 3H), 7.02 (t, J = 7.2 Hz, 1H), 7.27–7.30 (m, 2H), 7.33–7.42 (m, 3H), 7.50–7.58 (m, 5H), 7.96 (d, J = 8.0 Hz, 1H), 8.04 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 24.1, 34.2, 114.8, 115.4, 118.9, 119.2, 120.8, 121.1, 122.9, 123.0, 124.1, 125.6, 125.8, 126.5, 126.7, 128.2, 128.9, 130.9, 136.4, 139.1, 142.5, 147.6 ppm; HRMS (ESI) calcd for $C_{25}H_{21}N$: 336.1752 (M+H$^+$), found: 336.1741.

*2-(1-(4-Methoxyphenyl)-3-vinylnaphthalen-2-yl)-N-methylaniline (**3b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.65 (s, 3H), 3.32 (s, 1H), 3.73 (s, 3H), 5.16 (d, J = 10.8 Hz, 1H), 5.78 (d, J = 17.6 Hz, 1H), 6.48–6.57 (m, 3H), 6.71–6.77 (m, 3H), 7.00 (dd, J = 8.0, 1.6 Hz, 1H), 7.05–7.10 (m, 2H), 7.31–7.35 (m, 1H), 7.44–7.48 (m, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 8.14 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 55.1, 109.6, 112.8, 113.1, 115.4, 116.5, 124.0, 125.2, 126.0, 126.2, 126.9, 128.1, 128.3, 130.3, 131.0, 132.1, 133.1, 133.3, 135.0, 135.6, 135.9, 140.0,

Table 2. Palladium-catalyzed reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene **1** with 2-alkynylbenzenamine **2**.



Entry	R^1	R^2,R^3,R^4	L	Yield [%][a] 3	4
1	H (**1a**)	H, Ph, Me (**2a**)	L4	31 (**3a**)	64 (**4a**)
			L7	71 (**3a**)	20 (**4a**)
2	H (**1a**)	H, *p*-$MeOC_6H_4$, Me (**2b**)	L4	42 (**3b**)	51 (**4b**)
			L7	82 (**3b**)	16 (**4b**)
3	H (**1a**)	H, *p*-MeC_6H_4, Me (**2c**)	L4	39 (**3c**)	31 (**4c**)
			L7	75 (**3c**)	19 (**4c**)
4	H (**1a**)	H, *p*-ClC_6H_4, Me (**2d**)	L4	35 (**3d**)	50 (**4d**)
			L7	75 (**3d**)	24 (**4d**)
5	H (**1a**)	H, 2-thiophenyl, Me (**2e**)	L4	27 (**3e**)	71 (**4e**)
			L7	74 (**3e**)	23 (**4e**)
6	H (**1a**)	H, cyclopropyl, Me (**2f**)	L4	trace	
			L7	trace	
7	H (**1a**)	Me, Ph, Me (**2g**)	L4	29 (**3f**)	59 (**4f**)
			L7	75 (**3f**)	19 (**4f**)
8	H (**1a**)	*i*Pr, Ph, Me (**2h**)	L4	27 (**3g**)	53 (**4g**)
			L7	54 (**3g**)	7 (**4g**)
9	H (**1a**)	Cl, Ph, Me (**2i**)	L4	43 (**3h**)	54 (**4h**)
			L7	73 (**3h**)	20 (**4h**)
10	H (**1a**)	CF_3, Ph, Me (**2j**)	L4	35 (**3i**)	50 (**4i**)
			L7	72 (**3i**)	9 (**4i**)
11	H (**1a**)	H, Ph, Bn (**2k**)	L4	25 (**3j**)	60 (**4j**)
			L7	50 (**3j**)	trace
12	H (**1a**)	H, Ph, Ac (**2l**)	L4	trace	
			L7	trace	
13	4,5-$(OMe)_2$ (**1b**)	H, Ph, Me (**2a**)	L4	15 (**3k**)	72 (**4k**)
			L7	50 (**3k**)	29 (**4k**)
14	5-OMe (**1c**)	H, Ph, Me (**2a**)	L4	10 (**3l**)	85 (**4l**)
			L7	40 (**3l**)	20 (**4l**)
15	5-Me (**1d**)	H, Ph, Me (**2a**)	L4	30 (**3m**)	58 (**4m**)
			L7	64 (**3m**)	7 (**4m**)
16	5-F (**1e**)	H, Ph, Me (**2a**)	L4	39 (**3n**)	50 (**4n**)
			L7	54 (**3n**)	41 (**4n**)

[a] Yield of isolated product based on 2-alkynylbenzenamine **2**. Bn = benzyl, Ac = acetyl.

146.9, 158.3 ppm; HRMS (ESI) calcd for $C_{26}H_{23}NO$: 366.1858 (M+H^+), found: 366.1849.

*6-Ethyl-11-(4-methoxyphenyl)-5-methyl-5H-indeno[1,2-c]quinoline (**4b**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (t, J = 7.2 Hz, 3H), 3.51 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.91 (s, 3H), 7.04–7.08 (m, 3H), 7.28–7.36 (m, 3H), 7.46–7.52 (m, 4H), 7.99 (d, J = 8.0 Hz, 1H), 8.09 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 24.1, 33.9, 55.4, 114.4, 114.8, 115.3, 118.9, 119.0, 120.8, 121.0, 122.8, 123.1, 124.0, 125.5, 125.7, 126.4, 128.2, 131.1, 131.8, 136.4, 142.8, 147.3, 158.4 ppm; HRMS (ESI) calcd for $C_{26}H_{23}NO$: 366.1858 (M+H^+), found: 366.1851.

*N-Methyl-2-(1-p-tolyl-3-vinylnaphthalen-2-yl)aniline (**3c**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 2.65 (s, 3H), 3.32 (s, 1H), 5.15 (dd, J_1 = 10.8, 1.2 Hz, 1H), 5.78 (dd, J = 17.6, 1.2 Hz, 1H), 6.47–6.56 (m, 3H), 6.77 (dd, J = 7.2, 1.2 Hz, 1H), 6.97–7.10 (m, 5H), 7.32 (dd, J = 6.8, 1.2 Hz, 1H), 7.43–7.47 (m, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.14 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 30.9, 109.6, 115.4, 116.5, 124.1, 125.3, 126.0, 126.2, 127.0, 128.1, 128.3, 128.4, 129.1, 130.9, 131.0, 133.0, 133.3, 134.8, 135.6, 135.7, 135.9, 136.2, 140.4, 147.0 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H^+), found: 350.1909.

*6-Ethyl-5-methyl-11-p-tolyl-5H-indeno[1,2-c]quinoline (**4c**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (t, J = 7.2 Hz, 3H), 2.50 (s, 3H), 3.56 (q, J = 7.2 Hz, 2H), 3.90 (s, 3H), 7.06–7.09 (m, 1H), 7.30–7.39 (m, 5H), 7.45–7.56 (m, 4H), 8.02 (d, J = 8.0 Hz, 1H), 8.11 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 21.5, 24.1, 33.9, 114.9, 115.2, 118.9, 119.4, 120.8, 121.0, 122.8, 124.0, 125.8, 126.4, 128.2, 129.6, 130.6, 135.8, 136.0, 136.4, 142.7, 147.3 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H^+), found: 350.1904.

*2-(1-(4-Chlorophenyl)-3-vinylnaphthalen-2-yl)-N-methylaniline (**3d**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.21 (s, 1H), 5.17 (dd, J = 10.8, 1.2 Hz, 1H), 5.79 (dd, J = 17.6, 1.2 Hz, 1H), 6.48–6.57 (m, 3H), 6.73 (dd, J = 7.2, 1.2 Hz, 1H), 7.03 (dd, J = 8.0, 2.0 Hz, 1H), 7.07–7.11 (m, 2H), 7.15 (dd, J = 8.0, 2.0 Hz, 1H), 7.19–7.21 (m, 1H), 7.32–7.36 (m, 1H), 7.44–7.49 (m, 2H), 7.91 (d, J = 8.4 Hz, 1H), 8.16 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.8, 109.7, 115.7, 116.6, 124.5, 124.7, 126.3, 126.4, 126.5, 127.7, 127.9, 128.3, 128.6, 130.6, 130.9, 132.3, 132.6, 132.8, 133.3, 134.9, 135.6, 137.3, 139.0, 146.8 ppm; HRMS (ESI) calcd for $C_{25}H_{20}ClN$: 370.1363 (M+H^+), found: 370.1369.

*11-(4-Chlorophenyl)-6-ethyl-5-methyl-5H-indeno[1,2-c]quinoline (**4d**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (t, J = 7.6 Hz, 3H), 3.55 (q, J = 7.6 Hz, 2H), 3.90 (s, 3H), 7.09–7.13 (m, 1H), 7.33–7.35 (m, 1H), 7.37–7.42 (m, 2H), 7.50–7.54 (m, 6H), 7.96 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 8.12 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 24.2, 33.9, 114.9, 115.5, 117.7, 118.6, 121.0, 121.1, 123.0, 124.2, 125.7, 125.8, 126.7, 129.1, 132.2, 132.3, 136.3, 137.5, 142.2, 147.7 ppm; HRMS (ESI) calcd for $C_{25}H_{20}ClN$: 370.1363 (M+H^+), found: 370.1358.

*N-Methyl-2-(1-(thiophen-3-yl)-3-vinylnaphthalen-2-yl)aniline (**3e**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.31 (s, 1H), 5.17 (dd, J = 12.4, 1.6 Hz, 1H), 5.78 (dd, J = 17.6, 1.6 Hz, 1H), 6.49–6.60 (m, 3H), 6.77 (d, J = 6.4 Hz, 1H), 6.87 (s, 1H), 6.98–6.99 (m, 1H), 7.09–7.14 (m, 2H), 7.34–7.39 (m, 1H), 7.45–7.49 (m, 1H), 7.68 (d, J = 6.0 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 8.15 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 109.6, 115.5, 116.5, 124.1, 124.3, 126.2, 126.3, 126.7, 128.2, 128.5, 133.0, 133.3, 135.6, 135.7 ppm; HRMS (ESI) calcd for $C_{23}H_{19}NS$: 342.1316 (M+H^+), found: 342.1318.

*6-Ethyl-5-methyl-11-(thiophen-3-yl)-5H-indeno[1,2-c]quinoline (**4e**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.50 (t, J = 7.6 Hz, 3H), 3.59 (q, J = 7.6 Hz, 2H), 3.97 (s, 3H), 7.16–7.19 (m, 2H), 7.23–7.32 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.45–7.49 (m, 1H), 7.53 (s, 1H), 7.77–7.78 (m, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 8.12 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9, 24.1, 35.1, 112.3, 113.9, 117.2, 118.6, 121.0, 121.4, 122.7, 123.4, 123.6, 124.0, 125.0, 126.1, 126.9, 127.3, 128.1, 130.3, 136.4, 138.6, 142.1, 149.3 ppm; HRMS (ESI) calcd for $C_{23}H_{19}NS$: 342.1316 (M+H^+), found: 342.1294.

*N,4-Dimethyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)aniline (**3f**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 3H), 2.63 (s, 3H), 3.17 (s, 1H), 5.17 (d, J = 10.8 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 6.39 (d, J = 8.0 Hz, 1H), 6.51–6.58 (m, 2H), 6.87 (d, J = 7.6 Hz, 1H), 7.06–7.23 (m, 5H), 7.32 (t, J = 8.0 Hz, 1H), 7.45–7.50 (m, 2H), 7.91 (d, J = 8.4 Hz, 1H), 8.16 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 31.2, 109.8, 115.4, 124.0, 125.1, 125.4, 126.0, 126.1, 126.8, 126.9, 127.2, 127.6, 128.1, 128.7, 129.3,

131.0, 131.7, 132.7, 133.2, 135.0, 135.5, 135.8, 138.8, 140,2, 144.8 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H^+), found: 350.1920.

*6-Ethyl-2,5-dimethyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4f**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (t, J = 7.6 Hz, 3H), 2.18 (s, 3H), 3.55 (q, J = 7.6 Hz, 2H), 3.88 (s, 3H), 7.17 (d, J = 8.4 Hz, 1H), 7.28–7.37 (m, 2H), 7.39–7.43 (m, 2H), 7.49–7.58 (m, 5H), 7.74 (s, 1H), 8.10 ppm (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 21.0, 24.1, 33.9, 109.3, 112.4, 114.6, 115.2, 118.8, 120.6, 120.9, 122.9, 123.9, 125.9, 126.5, 127.6, 128.2, 128.7, 130.8, 132.3, 134.4, 139.0, 142.4, 147.3 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H^+), found: 350.1905.

*4-Isopropyl-N-methyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)aniline (**3g**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, J = 7.2 Hz, 6H), 2.60–2.65 (m, 4H), 3.22 (s, 1H), 5.18 (d, J = 11.2 Hz, 1H), 5.82 (d, J = 17.6 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.56–6.63 (m, 2H), 6.90 (dd, J = 8.4, 2.0 Hz, 1H), 7.01–7.02 (m, 1H), 7.14–7.24 (m, 4H), 7.33 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.17 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8, 24.5, 31.2, 33.1, 109.5, 115.4, 123.9, 125.0, 125.9, 126.0, 126.1, 126.6, 126.7, 126.9, 127.1, 127.7, 128.1, 129.3, 129.4, 131.1, 133.2, 135.4, 135.4, 135.8, 136.8, 139.0, 145.1 ppm; HRMS (ESI) calcd for $C_{28}H_{27}N$: 378.2222 (M+H^+), found: 378.2220.

*6-Ethyl-2-isopropyl-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4g**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, J = 6.8 Hz, 6H), 1.53 (t, J = 7.6 Hz, 3H), 2.69–2.76 (m, 1H), 3.49 (q, J = 7.6 Hz, 2H), 3.81 (s, 3H), 7.19–7.21 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.34–7.42 (m, 3H), 7.50–7.59 (m, 5H), 7.84 (d, J = 2.0 Hz, 1H), 8.08 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 23.8, 24.0, 33.4, 34.2, 114.5, 115.2, 118.8, 118.9, 120.6, 121.0, 122.9, 123.0, 123.9, 125.6, 126.0, 126.5, 128.3, 128.8, 131.0, 134.5, 139.3, 142.4, 143.3, 147.4 ppm; HRMS (ESI) calcd for $C_{28}H_{27}N$: 378.2222 (M+H^+), found: 378.2218.

*4-Chloro-N-methyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)aniline (**3h**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 3.32 (s, 1H), 5.19 (d, J = 11.2 Hz, 1H), 5.80 (d, J = 17.2 Hz, 1H), 6.36 (d, J = 8.8 Hz, 1H), 6.47–6.54 (m, 1H), 6.76 (d, J = 2.0 Hz, 1H), 7.00 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H), 7.05–7.06 (m, 1H), 7.14–7.20 (m, 3H), 7.25–7.35 (m, 2H), 7.45–7.50 (m, 2H), 7.90 (d, J = 8.0 Hz, 1H), 8.15 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 110.6, 116.0, 121.0, 124.4, 126.3, 126.5, 126.5, 126.9, 127.1, 127.6, 127.7, 128.1, 128.2, 129.0, 130.6, 131.0, 132.7, 133.3, 133.4, 135.2, 135.4, 138.4, 140.5, 145.6 ppm; HRMS (ESI) calcd for $C_{25}H_{20}ClN$: 370.1363 (M+H^+), found: 370.1360.

*2-Chloro-6-ethyl-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4h**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (t, J = 8.0 Hz, 3H), 3.42 (q, J = 8.0 Hz, 2H), 3.75 (s, 3H), 7.20–7.23 (m, 1H), 7.30–7.33 (m, 2H), 7.36 (d, J = 7.2 Hz, 1H), 7.44–7.45 (m, 1H), 7.53–7.54 (m, 5H), 7.87 (d, J = 2.0 Hz, 1H), 8.05 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5, 24.0, 34.4, 116.7, 119.2, 120.3, 121.1, 121.3, 124.2, 124.2, 124.3, 124.9, 126.3, 127.0, 128.2, 128.3, 129.1, 130.5, 134.9, 138.1, 142.3, 147.4 ppm; HRMS (ESI) calcd for $C_{25}H_{20}ClN$: 370.1363 (M+H^+), found: 370.1361.

*N-Methyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)-4-(trifluoromethyl)aniline (**3i**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (d, J = 5.2, 3H), 3.66 (q, J = 5.2, 1H), 5.19 (d, J = 11.2 Hz, 1H), 5.82 (d, J = 17.2 Hz, 1H), 6.43–6.53 (m, 2H), 7.00–7.02 (m, 2H), 7.13–7.20 (m, 3H), 7.22–7.29 (m, 2H), 7.32–7.36 (m, 1H), 7.47–7.51 (m, 2H), 7.92 (d, J = 8.4 Hz, 1H), 8.17 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.4, 108.5, 116.1, 123.7, 124.4, 124.5, 124.6, 125.1 (q, J_{CF} = 269.2 Hz), 125.7 (q, J_{CF} = 4.8 Hz), 126.3, 126.6, 127.0, 127.1, 127.6, 127.6, 128.2, 128.4 (q, J_{CF} = 3.8 Hz), 128.8, 130.9, 132.7, 133.2, 133.5, 135.1, 135.2, 138.4, 140.8, 149.3 ppm; HRMS (ESI) calcd for $C_{26}H_{20}F_3N$: 404.1626 (M+H^+), found: 404.1615.

*6-Ethyl-5-methyl-11-phenyl-2-(trifluoromethyl)-5H-indeno[1,2-c]quinoline (**4i**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (t, J = 7.2 Hz, 3H), 3.53 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 7.36–7.45 (m, 2H), 7.53–7.55 (m, 8H), 8.11 (d, J = 7.6 Hz, 1H), 8.19 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 24.1, 34.5, 115.5, 115.8, 119.3, 121.2, 121.6, 122.6, 122.7, 122.9 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 269.8 Hz), 124.7, 127.2, 128.3, 129.1, 130.2, 130.4, 137.8, 138.4, 142.6, 147.3 ppm; HRMS (ESI) calcd for $C_{26}H_{20}F_3N$: 404.1626 (M+H^+), found: 404.1621.

*N-Benzyl-2-(1-phenyl-3-vinylnaphthalen-2-yl)aniline (**3j**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 1H), 4.20 (s, 2H), 5.21 (d, J = 10.8 Hz, 1H), 5.83 (d, J = 17.2 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.54–6.55 (m, 2H), 6.80 (d, J = 7.2 Hz, 1H), 6.97–7.01 (m, 2H), 7.15–7.26 (m, 9H), 7.45–7.50 (m, 3H), 7.91 (d, J = 7.6 Hz, 1H), 8.17 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.1, 67.1, 110.1, 115.5, 116.6, 124.2, 124.9, 126.1, 126.2, 126.9, 127.0, 127.2, 127.3, 127.6, 128.1, 128.2, 128.3, 128.5, 129.5, 131.1, 131.3, 132.7, 133.3, 134.7, 135.5, 135.9, 139.7, 140.4, 145.5 ppm; HRMS (ESI) calcd for $C_{31}H_{25}N$: 412.2065 (M+H^+), found: 412.2067.

*5-Benzyl-6-ethyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4j**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (t, J = 7.2 Hz, 3H), 3.44 (q, J = 7.2 Hz, 2H), 5.60 (s, 2H), 7.01 (t, J = 7.2 Hz, 1H), 7.16–7.24 (m, 3H), 7.30–7.45 (m, 7H), 7.52–7.60 (m, 5H), 7.97 (d, J = 8.0 Hz, 1H), 8.11 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.1, 24.2, 50.1, 115.1, 116.4, 119.0, 119.9, 121.1, 121.2, 123.0, 123.1, 124.4, 125.5, 125.6, 125.9, 126.6, 126.7, 127.7, 128.2, 128.9, 129.2, 130.8, 135.8, 136.8, 138.9, 142.9, 147.6 ppm; HRMS (ESI) calcd for $C_{31}H_{25}N$: 412.2065 (M+H^+), found: 412.2048.

*2-(6,7-Dimethoxy-1-phenyl-3-vinylnaphthalen-2-yl)-N-methylaniline (**3k**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.36 (s, 1H), 3.70 (s, 3H), 3.83 (s, 3H), 5.11 (d, J = 10.8 Hz, 1H), 5.74 (d, J = 17.2 Hz, 1H), 6.46–6.54 (m, 3H), 6.75–6.79 (m, 2H), 7.04–7.08 (m, 2H), 7.17–7.25 (m, 5H), 8.04 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 55.7, 56.0, 105.6, 106.4, 109.4, 114.3, 116.3, 122.5, 125.3, 126.8, 127.4, 127.6, 128.2, 128.5, 129.1, 129.2, 130.8, 131.2, 133.1, 133.8, 134.7, 135.8, 138.8, 147.0, 149.5, 149.8 ppm; HRMS (ESI) calcd for $C_{27}H_{25}NO_2$: 396.1964 (M+H^+), found: 396.1961.

*6-Ethyl-8,9-dimethoxy-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4k**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (t, J = 7.2 Hz, 3H), 3.43 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.88 (s, 3H), 4.00 (s, 3H), 6.99 (s, 1H), 7.00–7.02 (m, 1H), 7.29–7.33 (m, 1H), 7.42–7.47 (m, 2H), 7.52–7.60 (m, 5H), 7.90 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5, 23.9, 34.2, 56.0, 57.1, 101.1, 105.7, 115.3, 118.9, 120.8, 121.8, 122.7, 122.9, 125.2, 125.9, 126.6, 129.0, 130.7, 132.2, 135.9, 137.1, 139.1, 145.3, 146.2, 148.3 ppm; HRMS (ESI) calcd for $C_{27}H_{25}NO_2$: 396.1964 (M+H^+), found: 396.1953.

*2-(6-Methoxy-1-phenyl-3-vinylnaphthalen-2-yl)-N-methylaniline (**3l**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.35 (s, 1H), 3.94 (s, 3H), 5.16 (d, J = 11.2 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 6.46–6.55 (m, 3H), 6.76 (dd, J = 7.2 Hz, 1H), 7.00 (dd, J = 9.2, 2.0 Hz, 1H), 7.04–7.08 (m, 2H), 7.13–7.19 (m, 3H), 7.20–7.24 (m, 2H), 7.41 (d, J = 9.2 Hz, 1H), 8.07 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9, 55.4, 105.8, 109.5, 115.4, 116.3, 118.8, 123.0, 125.1, 126.8, 127.3, 127.5, 128.2, 128.5, 129.1, 130.9, 131.2, 132.5, 135.9, 136.0, 138.9, 147.1, 157.9 ppm; HRMS (ESI) calcd for $C_{26}H_{23}NO$: 366.1858 (M+H^+), found: 366.1860.

*6-Ethyl-8-methoxy-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4l**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (t, J = 8.0 Hz, 3H), 3.41 (q, J = 8.0 Hz, 2H), 3.79 (s, 3H), 3.91 (s, 3H), 6.99–7.03 (m, 2H), 7.28–7.31 (m, 1H), 7.40–7.42 (m, 3H), 7.49–7.57 (m, 4H), 7.66 (s, 1H), 7.90 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 24.0, 34.2, 56.2, 106.8, 111.5, 114.7, 115.3, 119.3, 122.8, 123.3, 124.4, 125.4, 126.2, 126.6, 128.8,

129.2, 130.8, 136.4, 137.2, 139.0, 147.6, 155.3 ppm; HRMS (ESI) calcd for $C_{26}H_{23}NO$: 366.1858 (M+H$^+$), found: 366.1855.

*N-Methyl-2-(6-methyl-1-phenyl-3-vinylnaphthalen-2-yl)aniline(**3m**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.65 (s, 3H), 3.32 (s, 1H), 5.13 (d, J = 11.2 Hz, 1H), 5.77 (d, J = 17.2 Hz, 1H), 6.45–6.55 (m, 3H), 6.75 (d, J = 7.2 Hz, 1H), 7.04–7.08 (m, 2H), 7.13–7.24 (m, 5H), 7.31 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 8.12 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.1, 30.9, 109.5, 115.0, 116.4, 123.9, 125.2, 125.7, 126.7, 127.3, 127.6, 128.1, 128.3, 128.5, 129.2, 131.0, 131.1, 131.5, 132.9, 134.6, 134.9, 135.8, 135.9, 139.0, 139.6, 146.9 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H$^+$), found: 350.1913.

*6-Ethyl-5,8-dimethyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4m**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (t, J = 7.6 Hz, 3H), 2.47 (s, 3H), 3.54 (q, J = 7.6 Hz, 2H), 3.89 (s, 3H), 7.01–7.05 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H); 7.29 (s, 1H), 7.33–7.37 (m, 1H), 7.41–7.44 (m, 1H), 7.49–7.57 (m, 5H), 7.92 (d, J = 8.0 Hz, 1H), 7.99 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 21.9, 24.1, 34.3, 115.2, 118.9, 120.8, 122.3, 122.7, 122.9, 125.8, 126.0, 126.4, 126.5, 128.8, 130.8, 133.9, 136.4, 139.1, 143.0, 146.6 ppm; HRMS (ESI) calcd for $C_{26}H_{23}N$: 350.1909 (M+H$^+$), found: 350.1904.

*2-(6-Fluoro-1-phenyl-3-vinylnaphthalen-2-yl)-N-methylaniline (**3n**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.66 (s, 3H), 3.30 (s, 1H), 5.18 (d, J = 11.2 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 6.46–6.55 (m, 3H), 6.74 (d, J = 7.2 Hz, 1H), 7.05–7.23 (m, 7H), 7.47–7.53 (m, 2H), 8.08 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.8, 109.6, 110.9 (d, $^2J_{CF}$ = 20.0 Hz), 116.2 (d, $^2J_{CF}$ = 23.9 Hz), 116.4, 123.4 (d, $^4J_{CF}$ = 4.8 Hz), 124.7, 127.0, 127.4, 127.7, 128.4, 129.1, 129.6 (d, $^3J_{CF}$ = 9.6 Hz), 129.8, 130.9, 131.0, 134.1(d, $^3J_{CF}$=9.5 Hz), 134.1, 135.5, 136.7, 138.6, 140.6, 146,9, 160.9 ppm (d, $^1J_{CF}$ = 246.0 Hz); HRMS (ESI) calcd for $C_{25}H_{20}FN$: 354.1658 (M+H$^+$), found: 354.1668.

*6-Ethyl-8-fluoro-5-methyl-11-phenyl-5H-indeno[1,2-c]quinoline (**4n**)*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.54 (t, J = 7.6 Hz, 3H), 3.41 (q, J = 7.6 Hz, 2H), 3.83 (s, 3H), 7.02–7.09 (m, 2H), 7.31–7.35 (m, 1H), 7.39–7.47 (m, 3H), 7.49–7.55 (m, 4H), 7.72 (dd, J_1 = 1.6 Hz, J_2 = 11.2 Hz, 1H), 7.92 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 24.0, 34.3, 107.1 (d, $^2J_{CF}$ = 24.8 Hz), 111.8 (d, $^2J_{CF}$ = 23.9 Hz), 115.4, 118.7, 119.4 (d, $^3J_{CF}$ = 9.6 Hz), 123.2 (d, $^4J_{CF}$ = 5.8 Hz), 125.5, 126.5, 126.7, 128.5 (d, $^3J_{CF}$ = 8.6 Hz), 128.9, 130.8, 136.3, 138.7, 138.7, 148.3, 159.2 ppm (d, $^1J_{CF}$ = 231.7 Hz); HRMS (ESI) calcd for $C_{25}H_{20}FN$: 353.1580 (M^+), found: 353.1586.

CCDC 857229 and CCDC 857230 contain the supplementary crystallographic data for for the structures **3a** and **4a**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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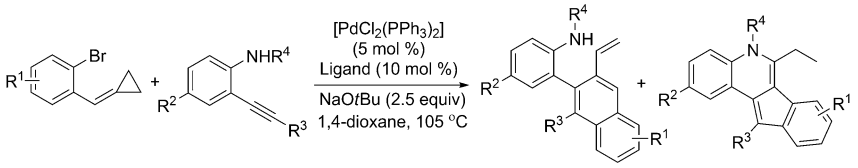

This way or that: A novel palladium-catalyzed domino reaction of 1-bromo-2-(cyclopropylidenemethyl)benzene and 2-alkynylbenzenamine is reported, which generates 2-(naphthalen-2-yl)benzenamines and 5*H*-indeno[1,2-*c*]quinolines via 6-*endo* and 5-*exo* cyclization, respectively. The regioselectivity for the final outcome can be affected by phosphine and N-heterocyclic carbene ligands.

Domino Reactions

Shaoyu Li, Yong Luo, Xiaocong Wang, Minjie Guo, Jie Wu** ——— ▮▮▮▮–▮▮▮▮

1-Bromo-2-(cyclopropylidenemethyl)-benzene: A Useful Building Block in the Palladium-Catalyzed Reaction of 2-Alkynylbenzenamine

