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Rhodium-catalyzed Oxidative Benzannulation of *N*-Pivaloylanilines with Internal Alkynes via Dual C–H Bond Activation: Synthesis of Highly Substituted Naphthalenes

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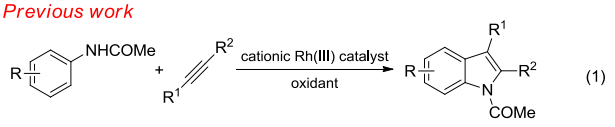
Abstract: An efficient method was developed for the synthesis of highly substituted naphthalenes through rhodium-catalyzed oxidative benzannulation of *N*-pivaloylanilines with internal alkynes. The benzannulation reaction proceeded smoothly via dual C–H bond activation to produce the corresponding highly substituted naphthalene products in satisfactory to good yields.

Introduction

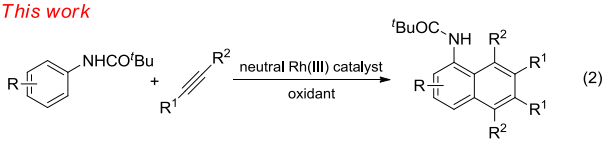
The transition-metal-catalyzed direct functionalization of C–H bonds recently emerged as an extremely powerful tool for the synthesis of complex organic molecules.[1] To control site selectivity in molecules that contain diverse C–H bonds, this method required appropriate directing groups such as heterocycles,[2] aminocarbonyl groups,[3] and acylamino groups[4] linked on the substrates. Among the directing groups employed, acylamino groups are frequently utilized because they can be easily installed into the substrates and converted to other functional groups.[5] For example, the acylamino groups linked on aromatic rings were successfully used as the directing groups for new carbon–carbon (including C_{aryl}–$C_{alkenyl}$[6], C_{aryl}–C_{aryl}[7], C_{aryl}–C_{alkyl}[8], and C_{aryl}–$C_{carbonyl}$[9]) and carbon–hetero atom (including C_{aryl}–N[10], C_{aryl}–O[11], C_{aryl}–B[12], C_{aryl}–Cl[13], C_{aryl}–Br[14], and C_{aryl}–I[15]) bond formation as well as for the carbocycle and heterocycle construction[16-18]. It was demonstrated that highly functionalized indoles can be efficiently synthesized through direct C–H bond functionalization in the presence of a cationic rhodium(III) catalyst using acetylamino group as the directing group (Eq. 1)[17a,17c,17e]. In the course of our recent studies on the transition-metal-catalyzed direct functionalization of C–H bonds, the regioselectivity in the reaction of *N*-aryl amides with internal alkynes is found to be easily turned by using a neutral rhodium(III) catalyst and a sterically hindered directing group (Eq.2). The results are reported in the current work.

Previous work



(1)

This work

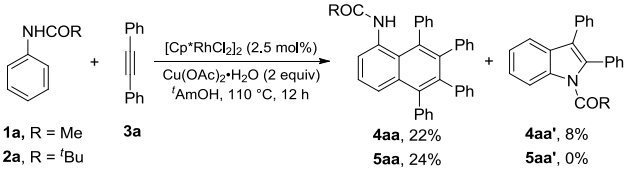


(2)

Results and Discussion

In the initial study, the reactions of *N*-phenylacetamide (**1a**) and *N*-phenylpivalamide (**2a**) were performed in the presence of $[Cp^*RhCl_2]_2$ as a precatalyst and $Cu(OAc)_2$ as an oxidant in *tert*-amyl alcohol (^{t}AmOH) at 110 °C for 12 h to investigate the effect of the steric hindrance of the directing group on the reaction regioselectivity (Scheme 1). The benzannulation product **4aa** was obtained in 22% yield along with an indole derivative **4aa'** in 8% yield from the reaction of **1a** with 1,2-diphenylethyne (**3a**).These results indicated that the benzannulation reaction could proceed in the presence of a neutral rhodium(III) catalyst. The subsequent investigation showed that the undesired indole forming reaction could be completely inhibited by installing a sterically hindered *tert*-butyl into the *N*-acyl group. The benzannulation product **5aa** was obtained in 24% yield as the sole product from the reaction of **2a** with **3a**. This result motivated us to optimize the reaction conditions for benzannulation using the neutral rhodium(III) catalyst and sterically hindered pivaloylamino group as the directing group.

Scheme 1. Effect of Steric Hindrance of Directing Group on Reaction Regioselectivity.



1a, R = Me
2a, R = ^{t}Bu

3a

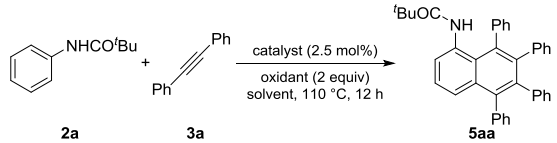
4aa, 22%
5aa, 24%

4aa', 8%
5aa', 0%

The benzannulation reaction of **2a** with **3a** was selected as a model to optimize the reaction conditions. Results are shown in Table 1. The use of $RhCl_3$ and $RhCl(PPh_3)_3$ as rhodium precatalysts instead of $[Cp^*RhCl_2]_2$ led to no reaction (entry 1 vs. entries 2 and 3). The solvents were then screened using polar [^{t}AmOH, acetone, 1,4-dioxane, and *N*,*N*-dimethyl formamide (DMF)] and nonpolar [toluene and 1,2-dichloroethane (DCE)] solvents (entries 1 and 4–8). DMF proved to be the best solvent among the solvents examined (entry 8, 58% yield).[19] The oxidants were finally screened using $[Cp^*RhCl_2]_2$ as a precatalyst and DMF as a solvent. $Cu(OAc)_2$ proved to be the best oxidant among the tested oxidants $Cu(OAc)_2$, $Cu(OTf)_2$, Ag_2CO_3, and AgOAc (entry 8 vs.entries 9–11). The yield of benzannulation product **5aa** was found to increase with increased $[Cp^*RhCl_2]_2$ loading (entry 12, 81%). Therefore, the subsequent benzannulation reactions of *N*-pivaloylanilines **2a**–

2p with internal alkynes **3a**–**3q** were performed in the presence of $[Cp^*RhCl_2]_2$ as a precatalyst and $Cu(OAc)_2$ as an oxidant in DMF at 110 °C for 12 h.

Table 1. Reaction Condition Screening[a]



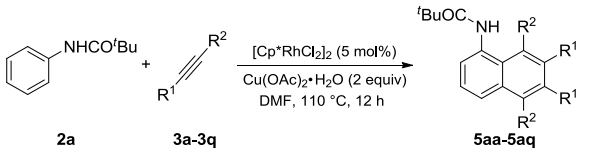
2a **3a** **5aa**

Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	^{t}AmOH	24
2	$RhCl_3$	$Cu(OAc)_2•H_2O$	^{t}AmOH	NR[c]
3	$RhCl(PPh_3)_3$	$Cu(OAc)_2•H_2O$	^{t}AmOH	NR[c]
4	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	Toluene	NR[c]
5	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	DCE	23
6	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	Acetone	40
7	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	1,4-dioxane	18
8	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	DMF	58
9	$[Cp^*RhCl_2]_2$	$Cu(OTf)_2$	DMF	NR[c]
10	$[Cp^*RhCl_2]_2$	Ag_2CO_3	DMF	NR[c]
11	$[Cp^*RhCl_2]_2$	AgOAc	DMF	3
12[d]	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2•H_2O$	DMF	81

[a]Reaction conditions: **2a** (0.25 mmol, 44.3 mg), **3a** (0.5 mmol, 89.1 mg), catalyst (2.5 mol%), oxidant (0.5 mmol, 2 equiv) in solvent (2.0 mL) at 110 °C for 12 h under N_2 atmosphere. [b]Isolated yield. [c]No reaction was observed; the starting materials were recovered. [d]5 mol% of $[Cp^*RhCl_2]_2$ was used.

The reactions of **2a** with various internal alkynes **3a**–**3q** were conducted under optimum conditions to explore the scope and limitation of the alkyne substrate, and the results are summarized in Table 2. The reactions of **2a** with diarylalkynes **3b**–**3f** bearing electron-withdrawing groups (F, Cl, and Br) on *para*- or *meta*-positions of benzene rings proceeded smoothly to provide the corresponding benzannulation products **5ab**–**5af** in moderate to good yields (entries 2–6, 63%–81% yields). The desired benzannulation product **5ag** was isolated in a satisfactory yield even when the diarylalkyne substrate **3g** bearing a strong electron-withdrawing group (CF_3) on *para*-positions of benzene rings (entry 7, 70% yield). The benzannulation products **5ah**, **5ai**, and **5ak**–**5am** were obtained in moderate yields (60%–67%) from the reactions of **2a** with diarylalkynes **3h**, **3i**, and **3k**–**3m** bearing electron-donating groups (Me and MeO) on *para*- or *meta*-positions of benzene rings (entries 8, 9, and 11–13). These abovementioned results indicated that the electronic property of the substituent linked on the benzene ring did not influence the reactivity of diarylalkyne. No reaction was observed when the diarylalkyne substrate, 1,2-di-*o*-tolylethyne (**3j**), was examined (entry 10). The non-reactivity of **3j** was considered to be due to the steric hindrance of the *ortho*-methyl substituent. The heterocycle-containing alkyne substrate, 1,2-di(thiophen-2-yl)ethyne (**3n**), was then tested, and the corresponding benzannulation product **5an** was isolated in 29% yield (entry 14). Surprisingly, when the unsymmetrical alkynes, 1-phenyl-1-propyne (**3o**), 1-phenyl-1-butyne (**3p**), and 1-phenyl-1-pentyne (**3q**), were finally examined under optimum conditions, the benzannulation products **5ao**–**5aq** were selectively obtained in moderate yields (57%–64%), and the generation of regioisomer was not observed at all. It was reported that no reaction was observed when this type of benzannulation was examined using *N*-acetylanilines and mono aryl- and alkyl-substituted internal alkynes as starting materials in the presence of palladium catalyst.[16]

Table 2. Substrate Scope of Internal Alkynes[a]



2a **3a-3q** **5aa-5aq**

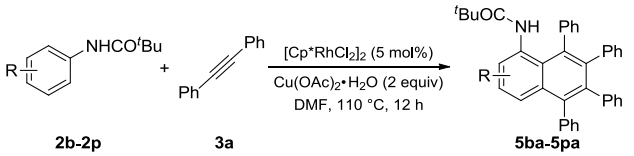
Entry	Internal Alkyne **3**		Product **5**	Yield (%)[b]
1	$R^1 = R^2$ = Ph	**3a**	**5aa**	81
2	$R^1 = R^2$ = 4-FC_6H_4	**3b**	**5ab**	63
3	$R^1 = R^2$ = 4-ClC_6H_4	**3c**	**5ac**	76
4	$R^1 = R^2$ = 4-BrC_6H_4	**3d**	**5ad**	81
5	$R^1 = R^2$ = 3-ClC_6H_4	**3e**	**5ae**	77
6	$R^1 = R^2$ = 3-BrC_6H_4	**3f**	**5af**	75
7	$R^1 = R^2$ = 4-$CF_3C_6H_4$	**3g**	**5ag**	70
8	$R^1 = R^2$ = 4-MeC_6H_4	**3h**	**5ah**	67
9	$R^1 = R^2$ = 3-MeC_6H_4	**3i**	**5ai**	67
10	$R^1 = R^2$ = 2-MeC_6H_4	**3j**	**5aj**	NR[c]
11	$R^1 = R^2$ = 4-$MeOC_6H_4$	**3k**	**5ak**	60
12	$R^1 = R^2$ = 3-$MeOC_6H_4$	**3l**	**5al**	67
13	$R^1 = R^2$ = 3,5-$Me_2C_6H_3$	**3m**	**5am**	62
14	$R^1 = R^2$ = 2-thienyl	**3n**	**5an**	29[d]
15	R^1 = Ph; R^2 = Me	**3o**	**5ao**	57
16	R^1 = Ph; R^2 = Et	**3p**	**5ap**	64
17	R^1 = Ph; R^2 = ^{n}Pr	**3q**	**5aq**	60

[a]Reaction conditions: **2a** (0.25 mmol, 44.3 mg), **3** (0.5 mmol, 2 equiv), $[Cp^*RhCl_2]^2$ (5 mol%, 7.8 mg), $Cu(OAc)_2·H_2O$ (0.50 mmol, 99.8 mg) in DMF (2.0 mL) at 110 °C for 12 h under N_2 atmosphere. [b]Isolated yield. [c]No reaction was observed, and the starting materials were recovered. [d]The starting material **2a** was recovered in 62% yield.

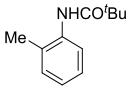
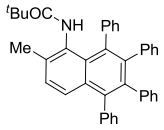
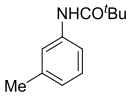
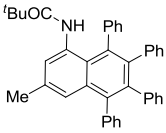
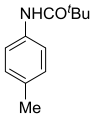
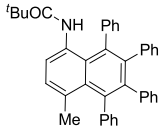
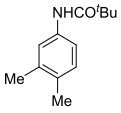
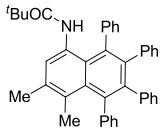
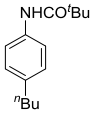
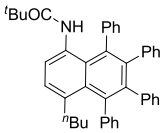
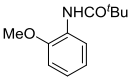
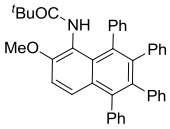
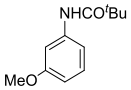
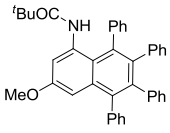
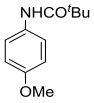
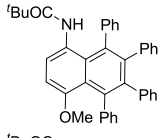
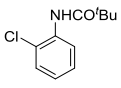
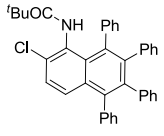
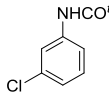
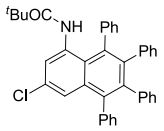
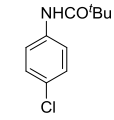
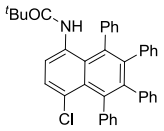
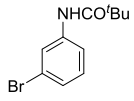
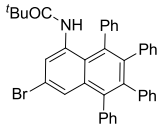
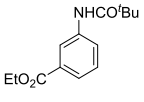
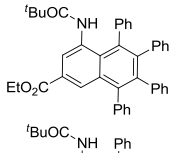
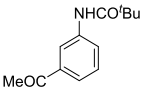
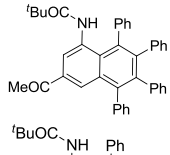
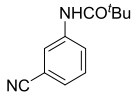
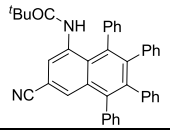
A series of *N*-pivaloylanilines were then examined with diphenylacetylene (**3a**) under the optimized reaction conditions to explore the scope and limitation of the *N*-pivaloylaniline substrate. The results are shown in Table 2. *N*-(*o*-tolyl)pivalamide (**2b**) and *N*-(*m*-tolyl)pivalamide (**2c**) presented different reactivity in the benzannulation reaction to give the corresponding products **5ba** and **5ca** in 50% and 79% yields, respectively (entries 1 and 2). These results indicated that the reactivity of the *N*-pivaloylaniline substrate is significantly influenced by the steric effect of the substituent linked on the benzene ring. Surprisingly, when methyl (Me) or normal butyl (^{n}Bu) were substituted at the *para*-positions of *N*-pivaloylaniline substrates, the desired benzannulation reaction could not take place. However, the hydroarylation reaction of diphenylacetylene occurred to furnish byproducts **6a**–**6c** (entries 3–5), which was considered to be produced from the steric hindrance of *para*-substituents Me and ^{n}Bu. Similarly, the reaction of the *N*-pivaloylaniline substrate **2g** that contains an *ortho*-methoxy group gives the benzannulation product **5ga** in a relatively low yield (60%) as the reaction of **2b** (entry 6). Good yields were observed in the reactions of *N*-pivaloylaniline substrates **2h** and **2i**, even when the methoxy group was linked on the *para*-position (entries 7 and 8). *N*-Pivaloylaniline substrates **2j**, **2k**, and **2l**, which bear a chloro atom on the *ortho*-, *meta*-, or *para*-positions, showed low reactivities in this type of benzannulation reaction to afford the corresponding products **5ja**–**5la** in low yields (entries 9–11, 25%–42%). Low yields were also observed in the reactions of *N*-pivaloylaniline substrates **2m**, **2n**, **2o**, and **2l** bearing electron-withdrawing groups (Br, CO_2Et, COMe, and

CN) on *meta*-positions (entries 12–15, 24%–41%).These abovementioned results indicated that the electronic property of the substituents strongly influenced the reactivities of *N*-pivaloylaniline substrates. All new products were identified through their NMR and HRMS data, as well as IR spectra. Product **5ao** was further identified by determining its X-ray structure.

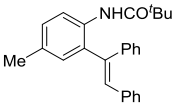
Table 3. Substrate Scope of *N*-pivaloylanilines[a]

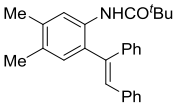


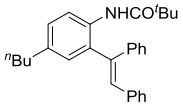
2b-2p **3a** **5ba-5pa**

Entry	*N*-pivaloylaniline**2**		Product **5**		Yield (%)[b]
1		**2b**		**5ba**	50
2		**2c**		**5ca**	79
3		**2d**		**5da**	0[c]
4		**2e**		**5ea**	0[d]
5		**2f**		**5fa**	0[e]
6		**2g**		**5ga**	60
7		**2h**		**5ha**	85
8		**2i**		**5ia**	88
9		**2j**		**5ja**	25[f]
10		**2k**		**5ka**	41
11		**2l**		**5la**	42
12		**2m**		**5ma**	41
13		**2n**		**5na**	39[g]
14		**2o**		**5oa**	35[h]
15		**2p**		**5pa**	24[i]

[a]Reaction conditions: **2** (0.25 mmol), **3a** (0.5 mmol, 89.1 mg), [Cp*RhCl$_2$]$_2$ (5 mol%, 7.8 mg), Cu(OAc)$_2$·H$_2$O (0.5 mmol, 99.8 mg) in DMF (2.0 mL) at 110 °C for 12 h under N_2 atmosphere. [b]Isolated yield. [c]By-product **6a** was separated in 20% yield, and the starting material **2d** was recovered in 63% yield. [d]By-product **6b** was separated in 30% yield, and the starting material **2e** was recovered in 56% yield. [e]By-product **6c** was separated in 39% yield, and the starting material **2f** was recovered in 49% yield. [f]The starting material **2j** was recovered in 70% yield. [g]The starting material **2n** was recovered in 55% yield. [h]The starting material **2o** was recovered in 60% yield. [i]The starting material **2p** was recovered in 70% yield.

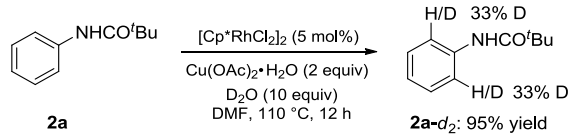

6a, 20%


6b, 30%

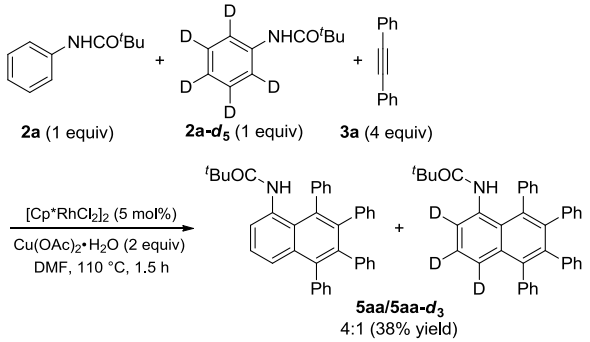

6c, 39%

To gain insight into the mechanism of this type of benzanulation reaction, a deuterium labeling experiment was conducted to investigate whether the reaction proceeded via the C–H bond activation pathway (Scheme 2). A significant amount of deuterium-labeled **2a-*d*$_2$** was observed when the *N*-pivaloylaniline substrate **2a** was treated without alkyne substrate under optimized reaction conditions in the presence of D_2O. This observation reveals that the target reactions indeed proceeded via the C–H bond activation pathway. Further study on the deuterium kinetic isotope effect (DKIE) by conducting an intermolecular competition reaction between **2a** and **2a-*d*$_5$** demonstrated that the cleavage of the C–H bond in **2a** is involved in the rate-determining step (Scheme 3).

Scheme 2. H–D Exchange Experiment on Amide Substrate **2a** in the Presence of D_2O.

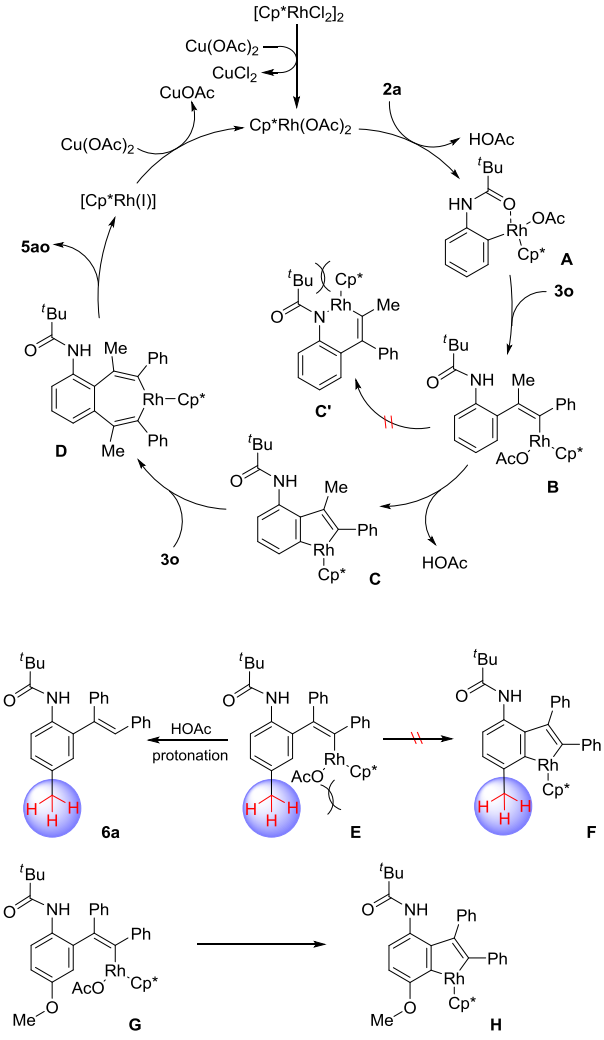


Scheme 3. Competition Experiments between **2a** and **2a-d_5**.



On the basis of our experimental outcomes and previous reports[18], a plausible catalytic cycle is proposed to account for the present catalytic benzannulation reaction (Scheme 4). The catalytic cycle starts from $Cp^*Rh(OAc)_2$, which is generated in situ from the ligand exchange reaction between $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$. The coordination of the oxygen atom of **2a** to rhodium catalyst species and subsequent *ortho* C–H bond activation would generate a six-membered rhodacyclic intermediate **A** with the liberation of an acetic acid molecule. The insertion of **3o** into the Rh–C bond would regioselectively occur to produce intermediate **B**; the regioselectivity might be due to the different electron densities and steric effects of alkyne substituents (Me and Ph)[20]. The intermediate **B** would subsequently undergo a second C–H bond activation to afford intermediate **C**. A second insertion of alkyne **3o** into the Rh–C bond in the intermediate **C** would also regioselectively occur to produce intermediate **D**, which would subsequently undergo reductive elimination to generate a highly substituted naphthalene product **5ao** and a Rh(I) species. The Rh(I) species would then be re-oxidized to active catalytic species $Cp^*Rh(OAc)_2$ by $Cu(OAc)_2$. The formation of intermediate **C'** is considered to be inhibited by the steric hindrance of the *tert*-butyl group. Consequently, the formation of the benzoindole product was inhibited.

The intermediate **E** derived from *N*-pivaloylaniline substrate **2d** could not proceed cyclorhodation to produce intermediate **F**, which was considered to be due to the strong steric hindrance between Me and Cp* groups. The protonation reaction of intermediate **E** with HOAc generated in situ would take place to provide by-product **6a**. For the case of the *N*-pivaloylaniline substrate **2i**, the rhodacyclic intermediate **H** would be generated due to the weak steric hindrance caused in intermediate **G**; thereby the desired benzannulation product **5ia** could be obtained in a good yield.



Scheme 4. Proposed Reaction Mechanism.

Conclusions

In summary, the regioselectivity in the reaction of *N*-aryl amides with internal alkynes was successfully controlled by using a neutral rhodium(III) catalyst and a sterically hindered directing group. The rhodium-catalyzed regioselective oxidative benzannulation reaction proceeded smoothly via a dual C–H bond cleavage under mild conditions with affordable and simple starting materials to produce highly-substituted naphthalenes in moderate-to-good yields. This new protocol shows good functional group tolerance and broad substrate scope.

Experimental Section

1.1. General information

All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker

Avance II-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The chemical shifts are reported in ppm downfield (*δ*) from TMS, the coupling constants *J* are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on silica gel (SiO_2 60, 200-300 meth). Melting points were determined using a micro-melting point apparatus and are uncorrected. $[Cp^*RhCl_2]_2$[21] and $RhCl(PPh_3)_3$[22] were prepared from $RhCl_3$•xH_2O following a literature procedure. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available without any further purification. The starting materials **2a**–**2p**,[23] and **3b**–**3n**[24] were prepared according to the known procedure.

1.2. Characterization of starting materials 2a–2p

***N*-pivaloylaniline (2a)**[25]**.** White solid (3.3 g, 93% yield); mp: 132–133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.53 (d, *J* = 7.6 Hz, 2H), 7.36 (bs, 1H), 7. 31 (dd, *J* = 8.0, 7.6 Hz, 2H), 7.10 (dd, *J* = 7.6, 7.2 Hz, 1H), 1.32 (s, 9H).

***N*-(o-tolyl)pivalamide (2b)**[26]**.** White solid (0.86 g, 90% yield); mp: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 8.0 Hz, 1H), 7.23–7.17 (m, 3H), 7.06 (dd, *J* = 7.6, 7.2 Hz, 1H), 2.26 (s, 3H), 1.34 (s, 9H).

***N*-(m-tolyl)pivalamide (2c)**[27]**.** White solid (0.87 g, 91% yield); mp: 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (s, 1H), 7.29–7.27 (m, 2H), 7. 20 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H).

***N*-(p-tolyl)pivalamide (2d)**[26]**.** White solid (0.87 g, 91% yield); mp: 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40 (d, *J* = 8.0 Hz, 2H), 7.29 (bs, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 1.30 (s, 9H).

***N*-(3,4-dimethylphenyl)pivalamide (2e)**[25]**.** Light yellow solid (0.92 g, 90% yield); mp: 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 (s, 1H), 7.24–7.21 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H), 1.30 (s, 9H).

***N*-(4-butylphenyl)pivalamide (2f).** White solid (1.04 g, 89% yield); mp: 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 6.8 Hz, 2H), 7.32 (bs, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.60–1.53 (m, 2H), 1.36–1.30 (m, 11H), 0.91 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 176.6, 139.0, 135.7, 128.9, 120.1, 39.7, 35.2, 33.8, 27.8, 22.4, 14.1; IR (KBr) *υ* (cm^{-1}) 3315, 2956, 2928, 1653, 1597, 1519, 1408, 1317, 825; HRMS (ESI) Calcd for $C_{15}H_{23}NONa$ 256.1677 $[M+Na]^+$, found 256.1679.

***N*-(2-methoxyphenyl)pivalamide (2g)**[27]**.** White solid (0.93 g, 90% yield); mp: 39–40 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.41 (d, *J* = 8.0 Hz, 1H), 8.13 (bs, 1H), 7.02 (dd, *J* = 8.0, 8.0 Hz, 1H), 6. 96 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 1.32 (s, 9H).

***N*-(3-methoxyphenyl)pivalamide (2h)**[27]**.** White solid (0.93 g, 90% yield); mp: 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (s, 1H), 7.35 (bs, 1H), 7.20 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 1.32 (s, 9H).

***N*-(4-methoxyphenyl)pivalamide (2i).** White solid (0.95 g, 92% yield); mp: 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41 (d, *J* = 8.8 Hz, 2H), 7.36 (bs, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 176.6, 156.4, 131.2, 122.1, 114.1, 55.6, 39.5, 27.7; IR (KBr) *υ* (cm^{-1}) 3306, 2967, 1647, 1601, 1536, 1513, 1478, 1412, 1314, 1233, 1170, 1035, 828; HRMS (ESI) Calcd for $C_{12}H_{17}NO_2Na$ 230.1157 $[M+Na]^+$, found 230.1166.

***N*-(2-chlorophenyl)pivalamide (2j)**[28]**.** White solid (0.88 g, 83% yield); mp: 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.42 (d, *J* = 8.4 Hz, 1H), 8.02 (bs, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7. 27 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 7.6 Hz, 1H), 1.35 (s, 9H).

***N*-(3-chlorophenyl)pivalamide (2k)**[26]**.** White solid (0.90 g, 85% yield); mp: 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.68 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.27 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 1.31 (s, 9H).

***N*-(4-chlorophenyl)pivalamide (2l)**[29]**.** White solid (0.90 g, 85% yield); mp: 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.48 (d, *J* = 8.8 Hz, 2H), 7.33 (bs, 1H), 7. 27 (d, *J* = 8.4 Hz, 2H), 1.31 (s, 9H).

***N*-(3-bromophenyl)pivalamide (2m)**[27]**.** White solid (1.08 g, 84% yield); mp: 137–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (dd, *J* = 2.0, 1.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 (bs, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 8.0, 8.0 Hz, 1H), 1.31 (s, 9H).

Ethyl 3-pivalamidobenzoate (2n)[26]. White solid (1.01 g, 81% yield); mp: 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.01 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.55 (bs, 1H), 7.39 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 9H).

***N*-(3-acetylphenyl)pivalamide (2o)**[29]. White solid (0.88 g, 80% yield); mp: 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.05 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.48 (bs, 1H), 7.43 (dd, *J* = 8.0, 7.6 Hz, 1H), 2.62 (s, 3H), 1.34 (s, 9H).

***N*-(3-cyanophenyl)pivalamide (2p).** White solid (0.84 g, 83% yield); mp: 91–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.57 (bs, 1H), 7.43–7.36 (m, 2H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 177.2, 139.1, 129.9, 127.7, 124.4, 123.3, 118.7, 113.0, 39.9, 27.6; IR (KBr) *υ* (cm^{-1}) 3356, 2969, 2231, 1665, 1587, 1535, 1480, 1423, 1167, 791, 682; HRMS (ESI) Calcd for $C_{12}H_{14}N_2ONa$ 225.1004 $[M+Na]^+$, found 225.1001.

1.3. General Procedure for Synthesis of highly substituted naphthalenes 5 from N-pivaloylanilines 2a–2p and internal alkynes 3a–3q

A mixture of *N*-pivaloylaniline (**2**, 0.25 mmol, 1 equiv.), internal alkyne (**3**, 0.50 mmol, 2.0 equiv.), $[Cp^*RhCl_2]_2$ (3.9 mg, 0.00625 mmol, 2.5 mol%), and $Cu(OAc)_2$•H_2O (99.8 mg, 0.50 mmol, 2.0 equiv.) were charged in a Schlenk tube equipped with a stir bar. Dry DMF (2.0 mL) was added and the mixture was stirred at 110 °C for 12 h under N_2 atmosphere. The mixture was then washed with H_2O (3 × 20 mL) and extracted with $CHCl_3$ (3 × 20 mL). The combined organic phase were dried with Na_2SO_4. All volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 10 : 1) to afford the corresponding highly substituted naphthalene product.

1.4. Characterization of highly substituted naphthalenes 4, 5 and by-products 6

***N*-(5,6,7,8-tetraphenylnaphthalen-1-yl)acetamide (4aa)**[16].
White solid (27.0 mg, 22% yield); mp: 146–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.95 (d, *J* = 5.9Hz, 1H), 7.50 (d, *J* = 6.8Hz, 1H), 7.40 (dd, *J* =

6.2, 6.7 Hz, 1H), 7.26–7.16 (m, 10H), 6.99 (bs, 1H), 6.85–6.73 (m, 10H), 1.40(s, 3H).

1-(2,3-diphenyl-1H-indol-1-yl)ethanone (4aa')[17a]**.**
White solid (6.3 mg, 8% yield); mp: 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.41–7.37 (m, 1H), 7.35–7.19(m, 11H), 1.99 (s, 3H).

***N*-(5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5aa).**
White solid (107.7 mg, 81% yield); mp: 159–160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.40 (dd, J = 8.2, 7.6 Hz, 1H), 7.24–7.14 (m, 11H), 6.82–6.74 (m, 8H), 6.64–6.62 (m, 2H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 142.3, 141.3, 140.5, 140.3, 139.9, 139.5, 139.0, 134.4, 134.2, 133.6, 131.3, 131.1, 128.5, 127.7, 127.2, 126.7, 126.5, 125.8, 125.6, 125.5, 125.3, 124.9, 39.4, 27.0; IR (KBr) υ (cm^{-1}) 3425, 3337, 3050, 3024, 1670, 1601, 1493, 1475, 1441, 1382, 1157, 910, 778, 736, 730, 698; HRMS (ESI) *m/z* Calcd for $C_{39}H_{34}NO$ 532.2640 $[M+H]^+$, found 532.2645.

***N*-(5,6,7,8-tetrakis(4-fluorophenyl)naphthalen-1-yl)pivalamide (5ab).**
White solid (95.1 mg, 63% yield); mp: 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 6.2 Hz, 1H), 7.48–7.41(m, 2H), 7.14–7.05(m, 5H), 6.96–6.89 (m, 4H), 6.68–6.65 (m, 2H), 6.59–6.56 (m, 6H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ176.9, 161.8 (d, $^1J_{C-F}$ = 246.7 Hz), 161.6 (d, $^1J_{C-F}$ = 244.7 Hz), 160.7 (d, $^1J_{C-F}$ = 243.9 Hz), 160.6 (d, $^1J_{C-F}$ = 244.2 Hz), 140.4, 138.9, 138.2, 137.80 (d, $^4J_{C-F}$ = 3.0 Hz) , 135.97 (d, $^4J_{C-F}$ = 2.9 Hz), 135.81 ($^4J_{C-F}$ = 2.6 Hz), 135.29 ($^4J_{C-F}$ = 3.0 Hz), 134.1 ($^2J_{C-F}$ = 20.5 Hz), 132.53 ($^3J_{C-F}$ = 7.8 Hz), 132.23 ($^3J_{C-F}$ = 7.6 Hz), 126.12 ($^2J_{C-F}$ = 19.1 Hz), 125.7, 125.66, 125.64, 125.56, 115.35(d, $^2J_{C-F}$ = 21.0 Hz), 114.84 (d, $^2J_{C-F}$ = 21.1 Hz), 114.1, 114.0, 113.9, 113.8, 39.2, 26.9; IR (KBr) υ (cm^{-1}) 3444, 3321, 2956, 2917, 2848, 1659, 1604, 1509, 1478, 1380, 1224, 1157, 1093, 1015, 909, 830, 816, 777, 758, 734; HRMS (ESI) *m/z* Calcd for $C_{39}H_{29}NONaF_4$ 626.2083 $[M+Na]^+$, found 626.2088.

***N*-(5,6,7,8-tetrakis(4-chlorophenyl)naphthalen-1-yl)pivalamide (5ac).**
White solid (127.2 mg, 76% yield); mp: 268–270 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 5.0, 3.7 Hz, 1H), 7.44–7.43 (m, 2H), 7.26–7.18 (m, 4H), 7.07 (dd, J = 10.0, 8.4 Hz, 4H), 6.92 (s, 1H), 6.89–6.86 (m, 4H), 6.64 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 0.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 140.1, 139.7, 138.7, 138.2, 138.0, 137.7, 137.6, 134.1, 134.0, 133.5, 133.4, 133.0, 132.3, 132.2, 132.0, 131.9, 128.6, 128.2, 127.4, 127.3, 126.5, 126.33, 126.31, 125.7, 39.3, 26.9; IR (KBr) υ (cm^{-1}) 3439, 3326, 2960, 2921, 2865, 1653, 1492, 1395, 1378, 1092, 1015, 908, 837, 771, 758, 734; HRMS (ESI) *m/z* Calcd for $C_{39}H_{29}NONaCl_4$ 690.0901 $[M+Na]^+$, found 690.0890.

***N*-(5,6,7,8-tetrakis(4-bromophenyl)naphthalen-1-yl)pivalamide (5ad).**
White solid (163.1 mg, 77% yield); mp: 272–274 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 3.6, 3.6Hz, 1H), 7.43 (d, J = 3.6Hz, 2H), 7.39 (d, J = 6.4Hz, 2H), 7.34 (d, J = 6.8Hz, 2H), 7.06–6.98 (m, 8H), 6.89 (s, 1H), 6.59 (d, J = 6.4Hz, 2H), 6.49 (d, J = 6.4Hz, 2H), 0.88 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 140.6, 139.5, 138.7, 138.6, 138.5, 138.2, 137.4, 134.1, 134.0, 133.6, 132.6, 132.4, 132.3, 131.5, 131.2, 130.4, 130.3, 126.6, 126.5, 126.3, 125.8, 121.6, 121.3, 120.4, 120.2, 39.3, 26.9; IR (KBr) υ (cm^{-1}) 3438, 3329, 2956, 2924, 2854, 1654, 1489, 1391, 1101, 1071, 1011, 908, 827, 774, 764, 732; HRMS (ESI) *m/z* Calcd for $C_{39}H_{29}NONaBr_4$ 865.8880 $[M+Na]^+$, found 865.8846.

***N*-(5,6,7,8-tetrakis(3-chlorophenyl)naphthalen-1-yl)pivalamide (5ae).**
White solid (135.6 mg, 81% yield); mp: 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 3.9, 3.8 Hz, 1H), 7.48–7.46 (m, 2H), 7.22–7.02 (m, 9H), 6.89–6.47 (m, 8H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 143.6, 141.3, 141.2 140.9, 139.6, 138.7, 137.3, 134.8, 134.6, 134.0, 133.9, 133.7, 133.30, 133.27, 133.2, 133.13, 133.10, 133.03, 132.96, 132.93, 132.88, 132.8, 131.1, 131.0, 130.84, 130.78, 129.72, 129.68, 129.3, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.7, 127.5, 126.8, 126.5, 126.3, 126.1, 125.9, 39.4, 27.1; IR (KBr) υ (cm^{-1}) 3441, 3318, 2963, 1656, 1594, 1564, 1479, 1407, 1373, 1091, 1077, 908, 884, 778, 758, 732, 699; HRMS (ESI) *m/z* Calcd for $C_{39}H_{29}NONaCl_4$ 690.0901 $[M+Na]^+$, found 690.0915.

***N*-(5,6,7,8-tetrakis(3-bromophenyl)naphthalen-1-yl)pivalamide (5af).**
White solid (158.9 mg, 75% yield); mp: 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 4.4, 4.3 Hz, 1H), 7.48 (d, J = 4.6 Hz, 2H), 7.40–7.31 (m, 4H), 7.20–6.49 (m, 13H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 143.8, 141.4, 141.3, 141.1, 139.5, 138.5, 137.2, 134.1, 133.9, 133.81, 133.78, 133.6, 133.5, 130.51, 130.47, 130.3, 129.90, 129.85, 129.7, 129.5, 129.3, 129.2, 129.1, 128.8, 128.7, 128.5, 128.4, 126.8, 126.4, 125.9, 125.8, 122.8, 122.7, 122.18, 122.15, 122.10, 122.05, 122.01, 121.96, 121.38, 121.35, 121.2, 121.1, 120.99, 120.96, 39.3, 27.0; IR (KBr) υ (cm^{-1}) 3440, 3321, 3060, 2958, 2925, 2868, 1661, 1592, 1559, 1477, 1403, 1374, 1215, 1161, 1070, 996, 884, 817, 804, 756, 721, 695; HRMS (ESI) *m/z* Calcd for $C_{39}H_{29}NONaBr_4$ 865.8880 $[M+Na]^+$, found 865.8918.

***N*-(5,6,7,8-tetrakis(4-(trifluoromethyl)phenyl)naphthalen-1-yl)pivalamide (5ag).**
White solid (140.6 mg, 70% yield); mp: 271–273 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.2 Hz, 1H), 7.54–7.44 (m, 6H), 7.29 (d, J = 7.9 Hz, 4H), 7.16–7.10 (m, 4H), 6.87 (d, J = 7.8 Hz, 2H), 6.83 (s, 1H), 6.75 (d, J = 7.8 Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 145.5, 143.1, 142.7, 139.4, 138.9, 137.2, 134.4, 134.0, 133.7, 131.4, 131.3, 131.1, 131.0, 129.9–127.9 (m), 127.5, 127.2, 126.8, 126.1, 125.5, 125.2, 125.1, 125.1, 124.3 (q, J_{C-F} = 3.0 Hz), 124.0 (q, J_{C-F} = 3.1 Hz), 122.7, 122.5, 39.3, 26.9; IR (KBr) υ (cm^{-1}) 3357, 2955, 2918, 2849, 1654, 1616, 1457, 1324, 1165, 1122, 1105, 1065, 1019, 846, 756; HRMS (ESI) *m/z* Calcd for $C_{43}H_{29}NONaF_{12}$ 826.1955 $[M+Na]^+$, found 826.1960.

***N*-(5,6,7,8-tetra-p-tolylnaphthalen-1-yl)pivalamide (5ah).**
White solid (98.5 mg, 67% yield); mp: 194–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 6.7 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 8.2, 7.8 Hz, 1H), 7.06–6.96 (m, 9H), 6.62–6.59 (m, 6H), 6.49 (d, J = 7.9 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 141.5, 139.4, 139.20, 139.17, 137.7, 137.4, 137.1, 136.6, 135.8, 134.44, 134.37, 134.30, 134.25, 133.5, 131.2, 131.1, 131.0, 129.1, 128.3, 127.3, 127.2, 125.43, 125.38, 124.2, 39.3, 26.9, 21.4, 21.3, 21.2; IR (KBr) υ (cm^{-1}) 3421, 3022, 2956, 2923, 2868, 1670, 1510, 1466, 1378, 1157, 1110, 1021, 817, 756, 744; HRMS (ESI) *m/z* Calcd for $C_{43}H_{41}NONa$ 610.3086 $[M+Na]^+$, found 610.3094.

***N*-(5,6,7,8-tetra-m-tolylnaphthalen-1-yl)pivalamide (5ai).**
White solid (98.5 mg, 67% yield); mp: 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H), 7.38 (dd, J = 8.1, 8.0 Hz, 1H), 7.10–6.92 (m, 8H), 6.72–6.38 (m, 8H), 2.25–2.14 (m, 6H), 2.01–1.94 (m, 6H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 142.2, 142.1, 141.5, 141.4, 140.3, 140.2, 139.9, 139.4, 139.33, 139.29, 139.0, 137.9, 137.8, 136.87, 136.85, 136.8, 135.7, 135.6, 135.49, 135.45, 135.4, 134.19, 134.15, 134.1, 133.5, 132.2, 132.1, 131.9, 128.4, 128.3, 128.24, 128.17, 128.0, 127.81, 127.75, 127.4, 127.3, 127.2, 126.3, 126.2, 126.1, 126.0, 125.7, 125.5, 125.4, 125.0, 124.1, 39.4, 26.9, 21.5, 21.2, 21.1; IR (KBr) υ (cm^{-1}) 3420, 3345, 3015, 2957, 2921, 2867, 1672, 1603, 1584, 1509, 1487, 1378, 1157, 1090, 779, 755, 733, 700; HRMS (ESI) *m/z* Calcd for $C_{43}H_{41}NONa$ 610.3086 $[M+Na]^+$, found 610.3088.

***N*-(5,6,7,8-tetrakis(4-methoxyphenyl)naphthalen-1-yl)pivalamide (5ak).**
White solid (97.8 mg, 60% yield); mp: 102–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.3 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.36 (dd, J = 8.2, 7.9 Hz, 1H), 7.32 (s, 1H), 7.08–7.03 (m, 4H), 6.78–6.72 (m, 4H), 6.62 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 8.6 Hz, 2H), 6.40–6.37 (m, 4H), 3.78 (s, 3H), 3.75 (s, 3H), 3.63 (s, 3H), 3.61 (s, 3H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 158.5, 158.0, 156.9, 141.5, 139.2, 134.5, 134.3, 134.1, 133.5, 133.2, 132.9, 132.4, 132.3, 132.12, 132.05, 132.0, 125.4, 125.2, 123.9, 113.9, 113.1, 112.1, 55.4, 55.2, 55.0, 54.9, 39.3, 27.0; IR (KBr) υ (cm^{-1}) 3416, 2956, 2835, 1675, 1609, 1511, 1463, 1285, 1244, 1176, 1107, 1033, 830, 801, 755, 733; HRMS (ESI) *m*/*z* Calcd for $C_{43}H_{41}NO_5Na$ 674.2882 $[M+Na]^+$, found 674.2897.

***N*-(5,6,7,8-tetrakis(3-methoxyphenyl)naphthalen-1-yl)pivalamide (5al).**
White solid (109.2 mg, 67% yield); mp: 101–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 1H), 7.57–7.54 (m, 1H), 7.41 (dd, J = 8.1, 7.9 Hz, 1H), 7.32 (s, 1H), 7.19–7.10 (m, 2H), 6.86–6.69 (m, 8H), 6.41–6.18 (m, 6H), 3.69–3.66 (m, 3H), 3.62–3.59 (m, 3H), 3.50–3.46 (m, 6H), 0.84 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 177.0, 159.51, 159.45, 158.94, 158.89, 158.12, 158.06, 143.4, 141.6, 141.5, 141.1, 140.7, 140.61, 140.57, 139.2, 138.3, 134.2, 134.0, 133.5, 129.5, 129.4, 128.63, 128.57, 127.6, 125.8, 125.6, 125.5, 125.1, 124.0, 123.9, 123.3, 116.5, 116.4, 116.1, 114.14, 114.08, 112.7, 112.0, 55.31, 55.26, 55.19, 55.15, 39.4, 27.0; IR (KBr) υ (cm^{-1}) 3420, 3000, 2956, 2834, 1672, 1600, 1578, 1486, 1465, 1427, 1376, 1284, 1246, 1214, 1159, 1045, 877, 756, 740, 697; HRMS (ESI) *m*/*z* Calcd for $C_{43}H_{41}NO_5Na$ 674.2882 $[M+Na]^+$, found 674.2870.

***N*-(5,6,7,8-tetrakis(3,5-dimethylphenyl)naphthalen-1-yl)pivalamide (5am).**
White solid (99.8 mg, 62% yield); mp: 206–208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 6.9 Hz, 1H), 7.62 (s, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.35 (dd, J = 8.2, 7.8 Hz, 1H), 6.80–6.77 (m, 5H), 6.72 (s, 1H), 6.39 (d, J = 11.5 Hz, 4H), 6.25 (s, 2H), 2.19 (s, 6H), 2.13 (s, 6H), 1.95 (s, 6H), 1.94 (s, 6H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 141.9, 141.6, 140.1, 139.8, 139.1, 138.9, 137.5, 136.4, 135.01, 134.96, 134.9, 133.9, 133.4, 129.0, 128.42, 128.35, 127.84, 127.75, 126.6, 126.5, 126.2, 125.1, 124.4, 123.1, 39.3, 26.7, 21.3, 21.2, 21.0; IR (KBr) υ (cm^{-1}) 3415, 3002, 2956, 2917, 2864, 1673, 1601, 1513, 1479, 1388, 1375, 1355, 1260, 1205, 1157, 907, 843, 773, 755, 735, 704; HRMS (ESI) *m*/*z* Calcd for $C_{47}H_{49}NONa$ 666.3712 $[M+Na]^+$, found 666.3729.

***N*-(5,6,7,8-tetra(thiophen-2-yl)naphthalen-1-yl)pivalamide (5an).**
Yellowish solid (40.3 mg, 29% yield); mp: 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.59 (s, 1H), 7.48 (dd, J = 8.1, 8.0 Hz, 1H), 7.34–7.31 (m, 2H), 7.05–6.91 (m, 6H), 6.66–6.63 (m, 2H), 6.54 (d, J = 3.0 Hz, 1H), 6.48 (d, J = 3.0 Hz, 1H), 0.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 142.6, 140.63, 140.56, 139.7, 136.4, 135.3, 135.1, 134.5, 133.6, 130.1, 129.9, 129.7, 129.4, 129.30, 129.26, 129.0, 127.8, 127.4, 126.99, 126.96, 126.7, 126.5, 126.1, 125.9, 125.6, 125.4, 124.3, 120.1, 39.6, 27.2; IR (KBr) υ (cm^{-1}) 3416, 3343, 2960, 2926, 2868, 1669, 1501, 1473, 1368, 1224, 1158, 909, 850, 834, 756, 732, 693; HRMS (ESI) *m*/*z* Calcd for $C_{31}H_{25}NONaS_4$ 578.0717 $[M+Na]^+$, found 578.0729.

***N*-(5,8-dimethyl-6,7-diphenylnaphthalen-1-yl)pivalamide (5ao).**
White solid (58.1 mg, 57% yield); mp: 198–200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.73 (s, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.52 (dd, J = 8.1, 7.8 Hz, 1H), 7.14–7.04 (m, 6H), 6.96–6.93 (m, 4H), 2.52 (s, 3H), 2.42 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 142.0, 141.9, 141.7, 139.6, 134.4, 134.2, 130.5, 130.2, 129.1, 129.0, 127.6, 127.4, 126.3, 126.1, 126.0, 125.5, 124.1, 39.5, 27.7, 22.2, 17.9; IR (KBr) υ (cm^{-1}) 3284, 2954, 2923, 2852, 1645, 1508, 1457, 1377, 1206, 748, 699; HRMS (ESI) *m*/*z* Calcd for $C_{29}H_{29}NONa$ 430.2147 $[M+Na]^+$, found 430.2139.

***N*-(5,8-diethyl-6,7-diphenylnaphthalen-1-yl)pivalamide (5ap).**
White solid (69.7 mg, 64% yield); mp: 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.0 Hz, 1H), 7.78 (s, 1H), 7.54–7.53 (m, 2H), 7.12–7.04 (m, 6H), 6.98–6.93 (m, 4H), 3.01 (q, J = 7.3 Hz, 2H), 2.83 (q, J = 7.4 Hz, 2H), 1.35 (s, 9H), 1.14 (t, J = 7.4 Hz, 3H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ177.3, 141.7, 141.5, 141.4, 139.4, 136.6, 134.5, 133.73, 133.71, 130.2, 130.1, 128.4, 128.1, 127.28, 127.25, 126.0, 125.3, 125.0, 39.5, 27.6, 25.6, 24.1, 16.9, 15.6; IR (KBr) υ (cm^{-1}) 3302, 2965, 2931, 2872, 1651, 1602, 1496, 1442, 1366, 1238, 1185, 1167, 909, 760, 739, 700; HRMS (ESI) *m*/*z* Calcd for $C_{31}H_{33}NONa$ 458.2460 $[M+Na]^+$, found 458.2465.

***N*-(6,7-diphenyl-5,8-dipropylnaphthalen-1-yl)pivalamide (5aq).**
White solid (69.5 mg, 60% yield); mp: 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.74 (s, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.50 (dd, J = 8.1, 7.5 Hz, 1H), 7.11–7.03 (m, 6H), 6.97–6.93 (m, 4H), 2.95 (t, J = 8.0 Hz, 2H), 2.75 (t, J = 8.1 Hz, 2H), 1.61–1.55 (m, 2H), 1.46–1.41 (m, 2H), 1.35 (s, 9H), 0.82 (t, J = 7.2 Hz, 3H), 0.64 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 142.0, 141.9, 141.7, 139.6, 135.4, 134.02, 133.98, 133.5, 130.5, 130.3, 128.4, 127.3, 126.0, 125.3, 124.8, 39.7, 34.6, 33.3, 27.8, 25.5, 24.7, 14.9, 14.4; IR (KBr) υ (cm^{-1}) 3299, 2959, 2929, 2870, 1652, 1601, 1496, 1466, 1442, 1367, 1239, 1255, 1183, 1167, 909, 753, 733, 700; HRMS (ESI) *m*/*z* Calcd for $C_{33}H_{37}NONa$ 486.2773 $[M+Na]^+$, found 486.2764.

***N*-(2-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ba).**
White solid (68.2 mg, 50% yield); mp: 230–232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 1H), 7.30–7.08 (m, 11H), 6.78–6.67 (m, 10H), 6.47 (s, 1H), 2.26 (s, 3H), 0.84 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 143.8, 141.5, 140.59, 140.56, 139.9, 139.1, 138.4, 135.9, 134.8, 132.9, 131.7, 131.4, 131.3, 131.1, 130.7, 129.7, 129.6, 129.2, 129.1, 128.4, 128.1, 127.6, 127.0, 126.54, 126.49, 126.4, 125.4, 125.1, 39.2, 27.1, 19.5; IR (KBr) υ (cm^{-1}) 3435, 3341, 2956, 2924, 2854, 1649, 1492, 1459, 1441, 1383, 1157, 1071, 1027, 829, 759, 737, 699; HRMS (ESI) *m*/*z* Calcd for $C_{40}H_{35}NONa$ 568.2616 $[M+Na]^+$, found 568.2635.

***N*-(3-methyl-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ca).**
White solid (107.8 mg, 79% yield); mp: 244–246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.25–7.13 (m, 12H), 6.81–6.73 (m, 8H), 6.63–6.61 (m, 2H), 2.38 (s, 3H), 0.80 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 142.2, 140.6, 140.4, 140.0, 139.0, 138.8, 135.6, 134.24, 134.17, 133.3, 131.3, 131.1, 128.3, 127.6, 127.1, 126.5, 126.4, 125.34, 125.29, 125.14, 125.06, 124.6, 124.5, 123.6, 39.3, 26.9, 21.7; IR (KBr) υ (cm^{-1}) 3421, 3343, 2955, 2923, 1669, 1507, 1494, 1457, 1441, 1400, 1165, 1071, 1027, 858, 757, 735, 698; HRMS (ESI) *m*/*z* Calcd for $C_{40}H_{35}NONa$ 568.2616 $[M+Na]^+$, found 568.2615.

***N*-(2-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ga).**
White solid (84.3 mg, 60% yield); mp: 259–261 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 9.4 Hz, 1H), 7.23–7.00 (m, 10H), 6.77–6.69 (m, 10H), 6.53 (s, 1H), 6.36 (s, 1H), 3.87 (s, 3H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 154.0, 143.3, 141.9, 140.6, 140.5, 139.9, 138.9, 137.2, 134.7, 131.6, 131.3, 131.2, 131.0, 130.9, 130.0, 129.8, 128.8, 128.5, 127.8, 127.6, 127.4, 126.5, 126.3, 126.1, 125.3, 125.0, 120.1, 113.4, 56.7, 39.0, 27.2; IR (KBr) υ (cm^{-1}) 3445, 3328, 3056, 3023, 2958, 2925, 2868, 1673, 1602, 1505, 1482, 1441, 1353, 1280, 1118, 756, 698;

HRMS (ESI) *m/z* Calcd for $C_{40}H_{35}NO_2Na$ 584.2565 $[M+Na]^+$, found 584.2569.

***N*-(3-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ha).** White solid (119.4 mg, 85% yield); mp: 184–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.4 Hz, 1H), 7.35(s, 1H), 7.22–7.12 (m, 10H), 6.82–6.74 (m, 9H), 6.63–6.61 (m, 2H), 3.70 (s, 3H), 0.78 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 157.0, 141.9, 140.6, 140.4, 140.1, 139.3, 139.0, 138.3, 135.2, 134.3, 131.4, 131.24, 131.19, 131.0, 128.5, 127.7, 127.3, 126.6, 126.5, 125.4, 125.1, 120.5, 114.7, 105.0, 55.3, 39.4, 27.0; IR (KBr) υ (cm^{-1}) 3420, 3056, 3022, 2960, 1674, 1618, 1513, 1493, 1442, 1401, 1356, 1261, 1204, 1178, 1166, 1146, 1069, 910, 756, 734, 699; HRMS (ESI) *m/z* Calcd for $C_{40}H_{35}NO_2Na$ 584.2565 $[M+Na]^+$, found 584.2587.

***N*-(4-methoxy-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ia).** White solid (123.6 mg, 88% yield); mp: 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 1H), 7.13 (s, 5H), 7.06–6.98 (m, 5H), 6.87 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.76 (s, 6H), 6.65 (d, *J* = 5.9 Hz, 2H), 6.58–6.57 (m, 2H), 3.34 (s, 3H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 155.6, 144.0, 142.6, 141.5, 140.39, 140.36, 139.8, 137.3, 134.4, 131.4, 131.2, 130.9, 129.6, 128.7, 128.3, 127.0, 126.8, 126.4, 126.33, 126.28, 125.5, 125.1, 124.9, 107.0, 56.0, 39.2, 27.0; IR (KBr) υ (cm^{-1}) 3437, 3327, 3056, 3022, 2956, 2926, 2868, 1663, 1601, 1573, 1493, 1460, 1441, 1366, 1260, 1129, 1071, 757, 736, 697; HRMS (ESI) *m/z* Calcd for $C_{40}H_{35}NO_2Na$ 584.2565 $[M+Na]^+$, found 584.2545.

***N*-(2-chloro-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ja).** White solid (35.4 mg, 25% yield); mp: 244–246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.1 Hz, 1H), 7.44 (d, *J* = 9.2 Hz, 1H), 7.30–7.26 (m, 3H), 7.20–6.98 (m, 8H), 6.89–6.71 (m, 9H), 6.69 (s, 1H), 6.64 (d, *J* = 6.8 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 142.9, 142.4, 140.2, 140.0, 139.6, 139.3, 139.2, 135.5, 133.1, 132.7, 131.6, 131.1, 130.9, 130.8, 130.7, 130.42, 130.36, 129.8, 128.4, 128.2, 127.8, 127.74, 127.66, 127.1, 126.81, 126.75, 126.6, 126.5, 126.4, 125.6, 125.3, 39.3, 27.1; IR (KBr) υ (cm^{-1}) 3441, 3322, 3057, 3023, 2958, 2925, 2869, 1672, 1599, 1491, 1442, 1214, 1160, 1072, 1023, 926, 793, 756, 737, 698; HRMS (ESI) *m/z* Calcd for $C_{39}H_{32}NONaCl$ 588.2070 $[M+Na]^+$, found 588.2086.

***N*-(3-chloro-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ka).** White solid (58.0 mg, 41% yield); mp: 213–215 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.38 (s, 1H), 7.24–7.13 (m, 10H), 6.82–6.78 (m, 6H), 6.74–6.72 (m, 2H), 6.62–6.60 (m, 2H), 0.78 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 141.6, 141.5, 140.2, 140.1, 140.0, 139.2, 138.9, 135.2, 134.8, 134.5, 131.8, 131.3, 131.2, 131.0, 128.7, 127.9, 127.6, 127.0, 126.8, 126.6, 125.7, 125.4, 123.9, 123.9, 123.7, 123.4, 39.5, 27.0; IR (KBr) υ (cm^{-1}) 3417, 3335, 3057, 3025, 2963, 2928, 2869, 1673, 1598, 1493, 1455, 1441, 1376, 1347, 1245, 1158, 1027, 909, 861, 733, 698; HRMS (ESI) *m/z* Calcd for $C_{39}H_{33}NOCl$ 566.2251 $[M+H]^+$, found 566.2300.

***N*-(4-chloro-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5la).** White solid (59.4 mg, 42% yield); mp: 205–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.4Hz, 1H), 7.51 (d, *J* = 6.4Hz, 1H), 7.18–7.12 (m, 6H), 7.08–7.03 (m, 5H), 6.81–6.78 (m, 6H), 6.63–6.62 (m, 2H), 6.55 (d, *J* = 4.8Hz, 2H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 141.6, 141.4, 141.31, 141.25, 140.0, 139.9, 137.8, 134.8, 133.0, 131.6, 131.2, 131.1, 130.8, 129.8, 129.2, 128.5, 127.4, 126.9, 126.6, 126.5, 126.3, 125.4, 124.3, 39.4, 27.0; IR (KBr) υ (cm^{-1}) 3426, 3332, 3056, 3021, 2956, 2924, 2853, 1669, 1600, 1492, 1458, 1442, 1363, 1326, 1215, 1028, 814, 758, 732, 696; HRMS (ESI) *m/z* Calcd for $C_{39}H_{32}NONaCl$ 588.2070 $[M+Na]^+$, found 588.2056.

***N*-(3-bromo-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5ma).** White solid (62.6 mg, 41% yield); mp: 252–254 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.36 (s, 1H), 7.24–7.12 (m, 10H), 6.81–6.71 (m, 8H), 6.62–6.60 (m, 2H), 0.78 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 141.6, 141.4, 140.1, 140.0, 139.9, 139.1, 138.8, 135.04, 134.96, 134.5, 131.2, 131.14, 131.10, 130.9, 128.6, 127.8, 127.6, 127.0, 126.7, 126.6, 126.4, 125.6, 125.4, 123.6, 120.0, 39.5, 26.9; IR (KBr) υ (cm^{-1}) 3416, 3056, 3023, 2962, 1671, 1590, 1492, 1441, 1370, 1345, 1156, 1073, 1027, 911, 889, 859, 753, 733, 697; HRMS (ESI) *m/z* Calcd for $C_{39}H_{32}NONaBr$ 632.1565 and 634.1545 $[M+Na]^+$, found 632.1574 and 634.1562.

Ethyl 5,6,7,8-tetraphenyl-4-pivalamido-2-naphthoate (5na). White solid (58.9 mg, 39% yield); mp: 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.28 (s, 1H), 7.22–7.15 (m, 11H), 6.82–6.73 (m, 8H), 6.63–6.62 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 166.5, 143.5, 141.7, 141.1, 140.1, 139.94, 139.86, 139.0, 134.6, 134.0, 133.7, 131.3, 131.0, 128.5, 128.2, 127.9, 127.8, 127.7, 127.4, 127.0, 126.8, 126.6, 125.7, 125.5, 124.0, 61.2, 39.4, 27.0, 14.4; IR (KBr) υ (cm^{-1}) 3283, 3057, 3024, 2960, 2928, 2869, 1719, 1649, 1493, 1463, 1441, 1403, 1273, 1235, 1173, 1102, 1028, 910, 769, 732, 697; HRMS (ESI) *m/z* Calcd for $C_{42}H_{37}NO_3Na$ 626.2671 $[M+Na]^+$, found 626.2662.

***N*-(3-acetyl-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5oa).** Yellowish solid (50.2 mg, 35% yield); mp: 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.12 (s, 1H), 7.28–7.16 (m, 11H), 6.83–6.74 (m, 8H), 6.63–6.62 (m, 2H), 2.49 (s, 3H), 0.81 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 177.2, 143.7, 141.5, 141.2, 140.0, 139.8, 139.0, 134.6, 134.4, 134.1, 133.7, 131.2, 131.02, 130.97, 128.5, 127.9, 127.8, 127.5, 127.1, 127.0, 126.8, 126.6, 125.7, 125.5, 122.6, 39.4, 27.0, 26.7; IR (KBr) υ (cm^{-1}) 3420, 3056, 3024, 2958, 2925, 2865, 1684, 1601, 1493, 1456, 1441, 1402, 1274, 1220, 1171, 910, 734, 698; HRMS (ESI) *m/z* Calcd for $C_{41}H_{35}NO_2Na$ 596.2565 $[M+Na]^+$, found 596.2565.

***N*-(3-cyano-5,6,7,8-tetraphenylnaphthalen-1-yl)pivalamide (5pa).** Yellow solid (33.4 mg, 24% yield); mp: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.83 (s, 1H), 7.43 (s, 1H), 7.25–7.20 (m, 8H), 7.12 (d, *J* = 6.4 Hz, 2H), 6.84–6.80 (m, 6H), 6.73–6.71 (m, 2H), 6.61–6.59 (m, 2H), 0.79 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 144.4, 140.85, 140.77, 140.3, 139.6, 139.5, 138.4, 135.1, 134.6, 133.6, 131.13, 131.08, 130.9, 130.8, 130.6, 128.8, 128.1, 127.9, 127.4, 126.9, 126.7, 126.4, 125.9, 125.7, 123.2, 119.1, 109.4, 39.6, 26.9; IR (KBr) υ (cm^{-1}) 3416, 3057, 3024, 2958, 2925, 2227, 1684, 1493, 1441, 1396, 1158, 1071, 1027, 735, 698; HRMS (ESI) *m/z* Calcd for $C_{40}H_{32}N_2ONa$ 579.2412 $[M+Na]^+$, found 579.2410.

***(E)*-*N*-(2-(1,2-diphenylvinyl)-4-methylphenyl)pivalamide (6a).** Colorless oil (18.5 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.41 (bs, 1H), 7.24–7.15 (m, 11H), 7.11 (s, 1H), 6.75 (s, 1H), 2.32 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 139.6, 138.8, 137.0, 134.5, 133.6, 133.2, 132.2, 131.6, 129.9, 129.5, 129.3, 128.9, 128.4, 128.3, 127.5, 121.9, 39.7, 27.5, 21.0; IR (neat) υ (cm^{-1}) 3429, 3055, 3022, 2958, 2925, 2867, 1684, 1588, 1513, 1492, 1445, 1301, 1157, 921, 822, 759, 697; HRMS (ESI) *m/z* Calcd for $C_{26}H_{27}NONa$ 392.1990 $[M+Na]^+$, found 392.2005.

***(E)*-*N*-(2-(1,2-diphenylvinyl)-4,5-dimethylphenyl)pivalamide (6b).** Colorless oil (28.8 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.38 (bs, 1H), 7.25–7.13 (m, 10H), 7.06 (s, 1H), 6.73 (s, 1H), 2.28 (s,

3H), 2.23 (s, 3H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 139.5, 139.0, 137.2, 137.1, 133.3, 132.3, 132.1, 131.9, 130.0, 129.5, 128.9, 128.4, 128.2, 127.3, 123.0, 39.7, 27.5, 19.9, 19.3; IR (neat) υ (cm^{-1}) 3429, 3055, 3021, 2960, 2925, 2867, 1684, 1574, 1516, 1491, 1479, 1448, 1400, 1200, 1166, 921, 881, 756, 710, 695; HRMS (ESI) *m/z* Calcd for $C_{27}H_{29}NONa$ 406.2147 $[M+Na]^+$, found 406.2156.

(*E*)-*N*-(4-butyl-2-(1,2-diphenylvinyl)phenyl)pivalamide (6c).
Colorless oil (40.1 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 1H), 7.39 (bs, 1H), 7.23–7.15 (m, 12H), 7.10 (d, *J* = 2.4 Hz, 1H), 6.76 (s, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.63–1.56 (m, 2H), 1.40–1.31 (m, 2H), 0.99 (s, 9H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 139.7, 138.7, 137.0, 134.4, 133.3, 132.1, 131.0, 130.0, 129.5, 128.9, 128.7, 128.4, 128.3, 127.4, 121.9, 39.7, 35.2, 33.8, 27.5, 22.5, 14.1; IR (neat) υ (cm^{-1}) 3430, 3056, 3022, 2956, 2929, 2869, 1686, 1586, 1513, 1445, 1412, 1300, 1158, 922, 759, 697; HRMS (ESI) *m/z* Calcd for $C_{29}H_{33}NONa$ 434.2460 $[M+Na]^+$, found 434.2451.

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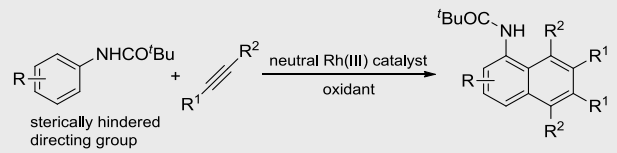

The regioselectivity in the reaction of *N*-aryl amides with internal alkynes could be easily turned by using a neutral rhodium(III) catalyst and sterically hindered directing group to prepare highly substituted naphthalenes.

Xuan Zhang, Xiaoqiang Yu, Xiujuan Feng, Yoshinori Yamamoto, Abdulrahman I. Almansour, Natarajan Arumugam, and Raju Suresh Kumar, Ming Bao**

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Rhodium-catalyzed Oxidative Benzannulation of *N*-Pivaloylanilines with Internal Alkynes via Dual C–H Bond Activation: Synthesis of Highly Substituted Naphthalenes