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Three-component coupling using arynes and isocyanides: straightforward access to benzo-annulated nitrogen or oxygen heterocycles

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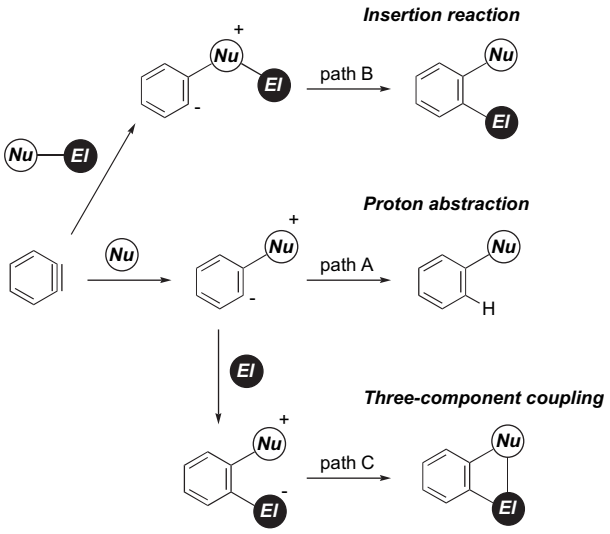
Dedicated to Professor Tamejiro Hiyama on the occasion of his 60th birthday

Abstract—A variety of aldehydes, ketones, benzoquinones, or sulfonylimines were found to couple with arynes and isocyanides, giving iminodihydroisobenzofuran or iminoisoindoline derivatives of structural diversity in a straightforward manner. Nucleophilic addition of isocyanides to arynes, a first step of the three-component coupling, was proved to be reversible by the reaction of an unsymmetrical aryne.

1. Introduction

Arynes are powerful and useful reactive intermediates in synthetic organic chemistry, which can be readily converted into polysubstituted arenes and benzo-annulated structures, being hardly accessible by conventional methods.[1] Because of the highly electrophilic character of arynes arising from their low-lying LUMO,[2] even neutral nucleophiles of diminished nucleophilicity facilely add to arynes to produce zwitterions, which act as key intermediates in nucleophilic coupling reactions (Scheme 1).[3] In general, the resulting aryl anion is apt to abstract a proton from the cationic site, resulting in the formation of monosubstituted arenes (path A).[4] On the other hand, we have recently reported on convenient and general method for introducing two functionalities into both ends of a triple bond of arynes via insertion reactions into a nucleophilic–electrophilic σ-bond, which proceed through intramolecular nucleophilic substitution (path B).[5,6] Similar double functionalization, being accompanied by cyclization, should also be achievable by three-component couplings through capturing the zwitterion with a third component (electrophile) (path C), and the couplings would be more attractive from a synthetic standpoint in gaining molecular complexity and diversity, however, there has been a limited number of reports in the literature,[7] probably because control of the reactivity of arynes is difficult. Herein we disclose that the three-component coupling of arynes occurs selectively by the use of isocyanides as nucleophiles.[8–10] By selecting suitable electrophiles, various benzo-annulated nitrogen or oxygen heterocycles can be fabricated in a straightforward manner.



Scheme 1.

2. Results and discussion

2.1. Three-component coupling of arynes, isocyanides, and aldehydes

First we carried out the reaction of benzyne, prepared in situ from 2-(trimethylsilyl)phenyl triflate (**1a**)[11] and a fluoride

Keywords: Aryne; Isocyanide; Nitrogen heterocycle; Oxygen heterocycle; Three-component coupling.
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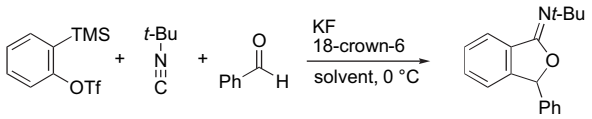
ion (KF/18-crown-6), with *tert*-butyl isocyanide (**2a**) and benzaldehyde (**3a**) in THF at 0 °C, and observed that a three-component coupling product, iminodihydroisobenzofuran **4a**, was produced in 46% yield (entry 1, Table 1).[12] The reaction also proceeded efficiently in 1,2-dimethoxyethane (DME, entry 2), whereas the use of diethyl ether or 1,4-dioxane as a solvent retarded the reaction (entries 3 and 4). The reaction using an equimolar amount of **1a** and **2a** gave only an 8% yield of **4a** (entry 5), and addition of excess **1a** did not improve the yield at all (entry 6).

Table 1. Three-component coupling of benzyne, *tert*-butyl isocyanide, and benzaldehyde[a]



1a : **2a** : **3a** — **4a**

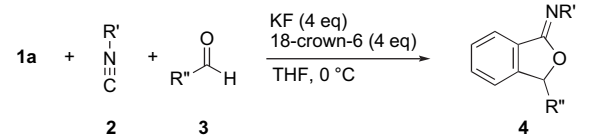
X : 1 : 2

Entry	*X*	Solvent	Time (h)	Yield[b] (%)
1	2	THF	2	46
2	2	DME	2	45
3	2	Et_2O	47	34
4[c]	2	Dioxane	6	12
5	1	THF	2	8
6	3	THF	5	44

[a] The reaction was carried out in a solvent (1 mL) at 0 °C using **1a**, **2a** (0.15 mmol), **3a** (0.30 mmol), KF, and 18-crown-6.
[b] Isolated yield based on **2a**.
[c] Room temperature.

Under the optimized reaction conditions, the three-component coupling using various isocyanides and aldehydes was next examined. As described in Table 2, 1-naphthaldehyde (**3b**) or 4-methoxybenzaldehyde (**3c**) also reacted with benzyne and **2a** to give the respective products (**4b** or **4c**) in moderate yields (entries 1 and 2). The reaction of 1,1,3,3-tetramethylbutyl isocyanide (*t*-OcNC, **2b**) was found to proceed more effectively, affording **4d**–**4f** in good yields (entries 3–5). In addition, an electron-deficient (**3d**), *meta*-substituted (**3e**), or sterically congested (**3f**) aldehyde could participate in the reaction to provide the variously substituted iminodihydroisobenzofurans (**4g**–**4i**, entries 6–8). The thienyl group in **3g** was compatible with the reaction conditions (entry 9),[13] and an aliphatic aldehyde (**3h** or **3i**) was also applicable to the reaction (entries 10 and 11). Besides **2a** and **2b**, 1-adamantyl isocyanide (**2c**) could participate in the reaction to afford the product in 77% yield (entry 12), whereas the reaction of sterically less congested cyclohexyl (**2d**) or *n*-octyl isocyanide (**2e**) resulted in the formation of a complex mixture.

Table 2. Three-component coupling of benzyne, isocyanides, and aldehydes[a]



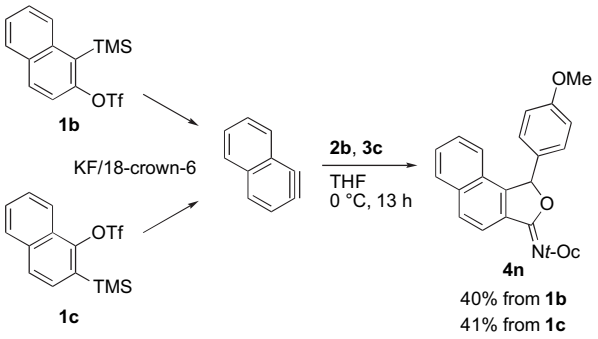
2 : **3** — **4**

2 : 1 : 2

Entry	R′		R″		Time (h)	Yield[b] (%)	Product
1	*t*-Bu	**2a**	1-Naphthyl	**3b**	5	49	**4b**
2	*t*-Bu	**2a**	4-$MeOC_6H_4$	**3c**	2	37	**4c**
3	*t*-Oc	**2b**	Ph	**3a**	7	65	**4d**
4	*t*-Oc	**2b**	1-Naphthyl	**3b**	5	73	**4e**
5	*t*-Oc	**2b**	4-$MeOC_6H_4$	**3c**	7	73	**4f**
6	*t*-Oc	**2b**	4-$CF_3C_6H_4$	**3d**	7	69	**4g**
7	*t*-Oc	**2b**	3-$MeOC_6H_4$	**3e**	5	65	**4h**
8	*t*-Oc	**2b**	2,4-$Me_2C_6H_3$	**3f**	5	61	**4i**
9	*t*-Oc	**2b**	2-Thienyl	**3g**	7	50	**4j**
10	*t*-Oc	**2b**	Et	**3h**	5	50	**4k**
11	*t*-Oc	**2b**	*t*-Bu	**3i**	7	40	**4l**
12	1-Ad	**2c**	4-$MeOC_6H_4$	**3c**	24	77	**4m**

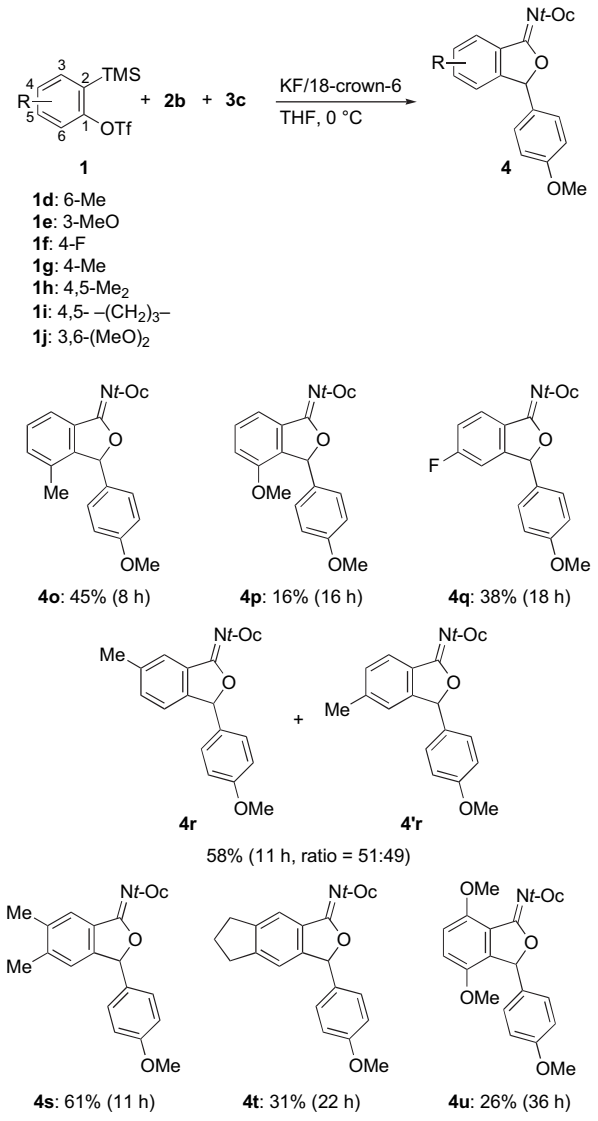
[a] The reaction was carried out in THF (1 mL) at 0 °C using **1a** (0.30 mmol), **2** (0.15 mmol), **3** (0.30 mmol), KF (0.60 mmol), and 18-crown-6 (0.60 mmol).
[b] Isolated yield based on **2**.

When 1-(trimethylsilyl)-2-naphthyl triflate (**1b**), a 1,2-naphthalyne precursor, was allowed to react with **2b** and **3c**, the imino moiety was selectively introduced into the 2-position of the naphthalene ring to give **4n** as the sole product (Scheme 2). Exclusive formation of **4n** was also observed in the reaction of 2-(trimethylsilyl)-1-naphthyl triflate (**1c**), which confirms the intermediacy of an aryne in the three-component coupling. Other substituted arynes could also be applied to the reaction. Thus, the reaction of 3-methylbenzyne (from **1d**) or 3-methoxybenzyne (from **1e**) took place with perfect regioselectivity, where the imino moiety was attached to the sterically less hindered position of the aryne (Scheme 3). A fluoro substituent at 4-position of an aryne (from **1f**) controlled the regioselectivity to afford **4q** solely, whereas the reaction of 4-methylbenzyne (from **1g**) furnished almost equal amounts of regioisomeric products **4r** and **4′r**. A 4,5-disubstituted aryne (from **1h** or **1i**) or sterically congested 3,6-dimethoxybenzyne (from **1j**) was also applicable to the reaction to give the corresponding iminodihydroisobenzofurans (**4s**–**4u**).

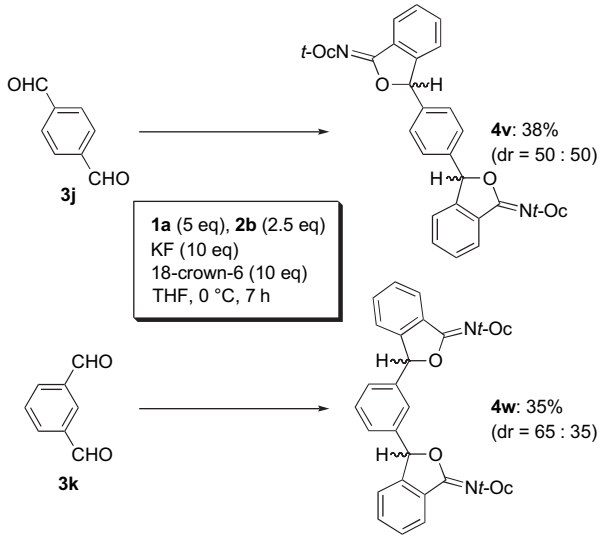


Scheme 2.

Furthermore, an aldehyde bearing two reaction sites can be employed for the three-component coupling. As depicted in Scheme 4, terephthalaldehyde (**3j**) reacted with benzyne and **2b** to afford a 38% yield of **4v** in 50:50 diastereomeric ratio, whereas the reaction of isophthalaldehyde (**3k**) gave a 65:35 ratio of the product (**4w**).



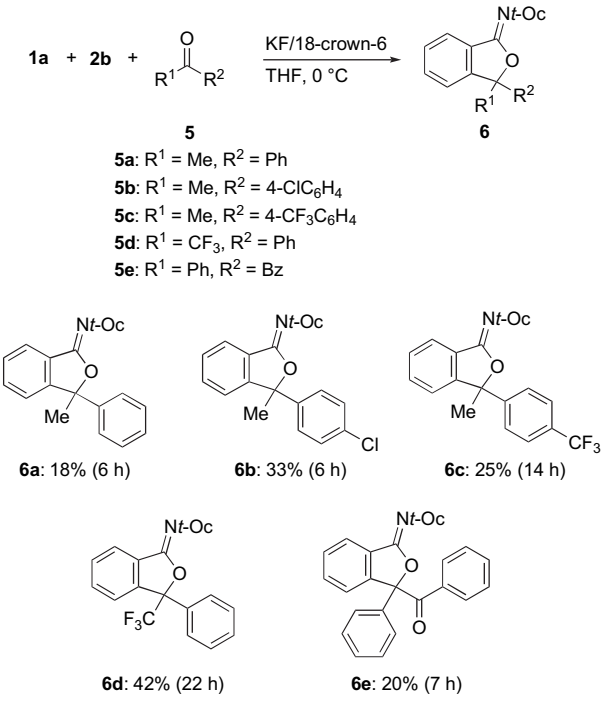
Scheme 3.



Scheme 4.

2.2. Three-component coupling of benzyne, isocyanides, and ketones

Similar to the case of aldehydes, several ketones could be used as electrophiles (Scheme 5). Thus, acetophenone (**5a**) was coupled with benzyne and **2b** to give the three-component coupling product (**6a**), although the yield was rather low, which should be ascribable to the reduced electrophilicity and steric hindrance of the carbonyl moiety. Introduction of such an electron-withdrawing group as chloro (**5b**) or trifluoromethyl (**5c**) into the 4′-position of an acetophenone increased the yield to some extent. Moreover, the reaction of trifluoroacetophenone (**5d**) afforded a 42% yield of **6d**, and benzil (**5e**), a 1,2-diketone, underwent the coupling to furnish **6e**.



Scheme 5.

In contrast, no trace of the three-component coupling product was obtained with 4′-methoxyacetophenone (**5f**), cyclohexanone (**5g**), benzophenone (**5h**), 2-butanone (**5i**), (*E*)-1,2-dibenzoylethene (**5j**), or 1,3-indandione (**5k**) (Chart 1).

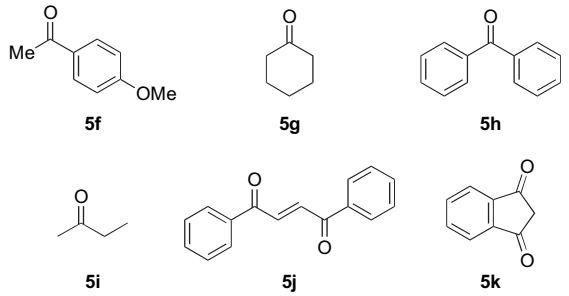
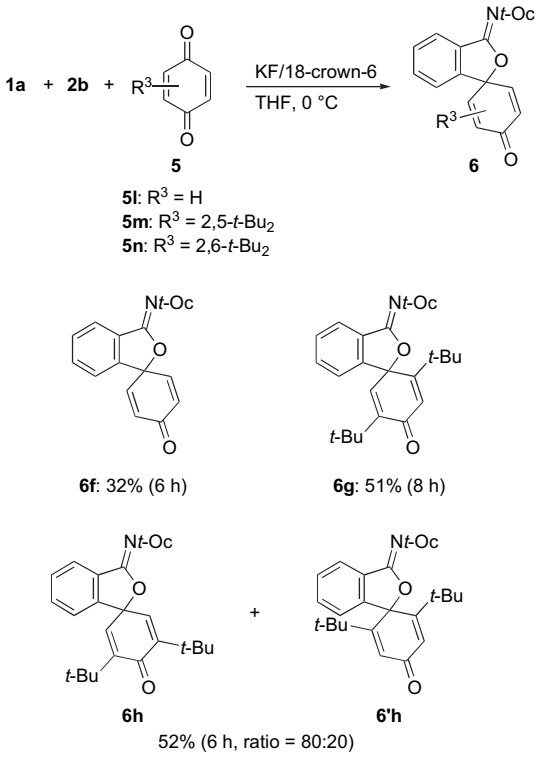


Chart 1.

2.3. Three-component coupling of benzyne, isocyanides, and benzoquinones

We next investigated the reaction of benzoquinones, because they can be regarded as electron-deficient ketones. As shown

in Scheme 6, treatment of benzoquinone **5l** with benzyne and **2b** provided a spiro type of iminodihydroisobenzofuran (**6f**). The reaction of di-*tert*-butylbenzoquinone (**5m** or **5n**) took place more smoothly, leading to the formation of the products in 51 or 52% yield, respectively. In the latter case, the predominant isomer was **6h** arising from cyclization at the less congested carbonyl group.



Scheme 6.

Unfortunately, the desired iminodihydroisobenzofurans were not formed at all in the reaction of other benzoquinones listed in Chart 2.

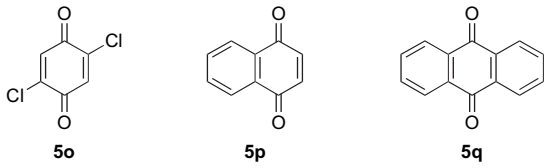
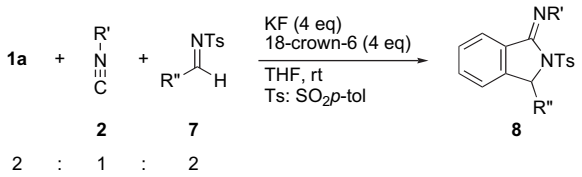


Chart 2.

2.4. Three-component coupling of arynes, isocyanides, and sulfonylimines

By changing electrophiles from carbonyl compounds to imines, the three-component coupling could also be utilized for direct synthesis of five-membered nitrogen heterocycles. When the reaction of *N*-tosylbenzaldimine (**7a**) with benzyne and **2b** was conducted in THF at room temperature, the three-component coupling product *N*-(3-phenyl-2-tosylisoindolinylidene)-*tert*-octylamine (**8a**) was formed in 64% yield (entry 1, Table 3). An electron-rich (**7b**), electron-deficient (**7c**), or sterically hindered (**7d–7f**) aldimine was also applicable to the reaction, giving the corresponding isoindolines (**8b–8f**) in modest to good yields (entries 2–6). In addition, the reaction of an aldimine bearing a thienyl moiety (**7g**) took place smoothly to provide **8g** in 64% yield (entry 7). Tertiary alkyl isocyanides (**2a** or **2c**), cyclohexyl (**2d**), or *n*-octyl isocyanide (**2e**) could also participate in the reaction to afford **8h–8k**, although the yields were relatively low (entries 8–11). As shown in Figure 1, configuration of the imine unit of the product has been determined to be *E* by an X-ray diffraction study of **8b**.[14]

Table 3. Three-component coupling of benzyne, isocyanides and sulfonylimines[a]



Entry	R′		R″		Time (h)	Yield[b] (%)	Product
1	*t*-Oc	**2b**	Ph	**7a**	5	64	**8a**
2	*t*-Oc	**2b**	4-$MeOC_6H_4$	**7b**	9	61	**8b**
3	*t*-Oc	**2b**	4-$CF_3C_6H_4$	**7c**	24	44	**8c**
4	*t*-Oc	**2b**	2,4-$Me_2C_6H_3$	**7d**	18	66	**8d**
5	*t*-Oc	**2b**	Mesityl	**7e**	24	68	**8e**
6	*t*-Oc	**2b**	1-Naphthyl	**7f**	19	59	**8f**
7	*t*-Oc	**2b**	2-Thienyl	**7g**	16	64	**8g**
8	*t*-Bu	**2a**	Ph	**7a**	19	55	**8h**
9	1-Ad	**2c**	Ph	**7a**	24	35	**8i**
10	Cy	**2d**	Ph	**7a**	6	23	**8j**
11	*n*-Oc	**2e**	Ph	**7a**	22	46	**8k**

[a] The reaction was carried out in THF (2 mL) at room temperature using **1a** (0.60 mmol), **2** (0.30 mmol), **7** (0.60 mmol), KF (1.2 mmol), and 18-crown-6 (1.2 mmol).
[b] Isolated yield based on **2**.

Variously substituted iminoisoindolines were accessible straightforwardly through the reaction of substituted arynes (Scheme 7). Thus, 4,5-disubstituted aryne (from **1h**, **1i**, or

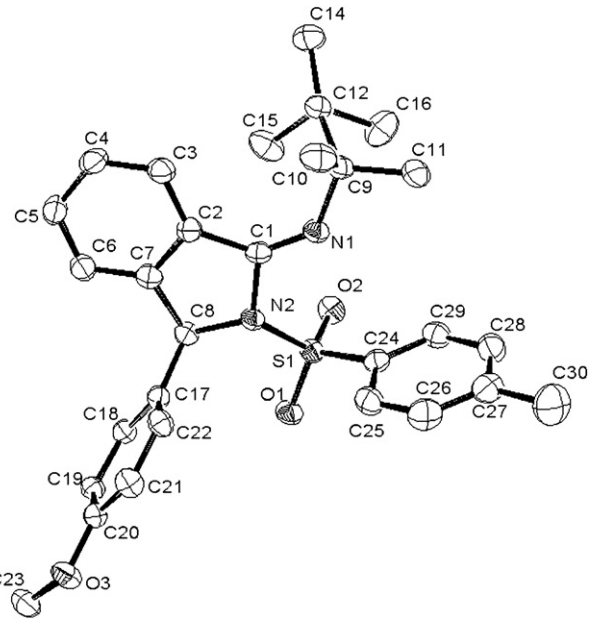
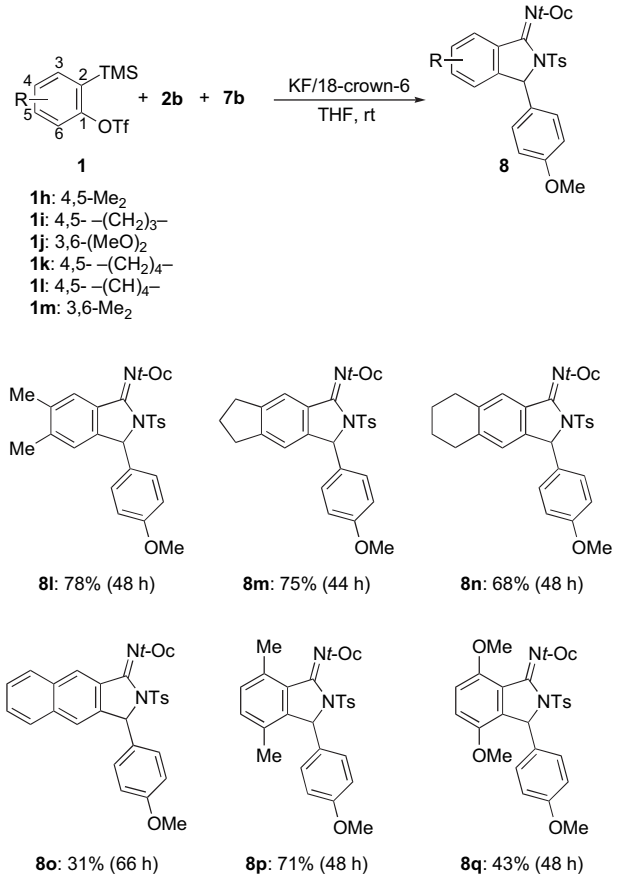


Figure 1.

1k) reacted efficiently with **2b** and **7b**, affording the corresponding product (**8l**–**8n**) in 78, 75, or 68% yield, whereas the reaction of 2,3-naphthalyne (from **1l**) resulted in a low yield of **8o**. Such a sterically congested aryne as 3,6-dimethylbenzyne (from **1m**) or 3,6-dimethoxybenzyne (from **1j**) could also be applied to the reaction, leading to the formation of the respective isoindoline (**8p** or **8q**) in 71 or 43% yield.

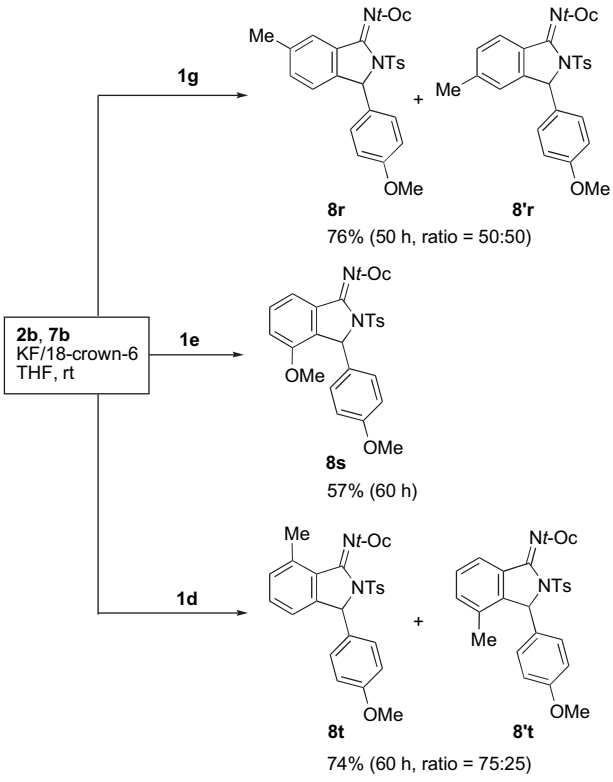


Scheme 7.

Furthermore, the three-component coupling of unsymmetrical arynes was carried out in order to clarify the regioselectivities (Scheme 8). When 4-methylbenzyne (from **1g**) was treated with **2b** and **7b**, an equal amount of regioisomers (**8r** and **8′r**) was produced in 76% yield, implying that the three-component coupling using sulfonylimines also proceeds through an aryne intermediate. The reaction of 3-methoxybenzyne (from **1e**) with **7b** took place with the same regioselectivity as that with **3c**, giving **8s** exclusively, where the imino moiety was introduced into the *meta* position of the methoxy group. In marked contrast, opposite regioselectivity to the case of **3c** was observed in the reaction of 3-methylbenzyne (from **1d**) with **7b** (**8t**/**8′t**=75:25), despite using the same isocyanide, which demonstrates that electrophiles govern the regioselectivities (cf. Scheme 3).

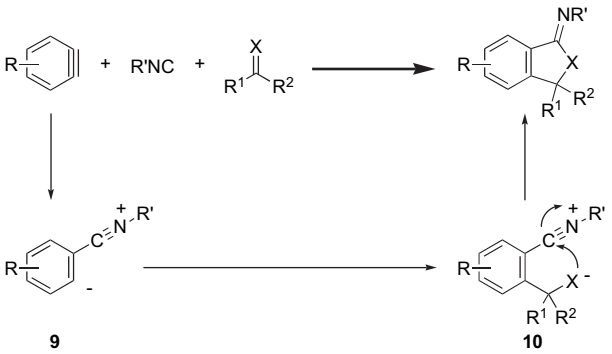
2.5. Reaction pathway

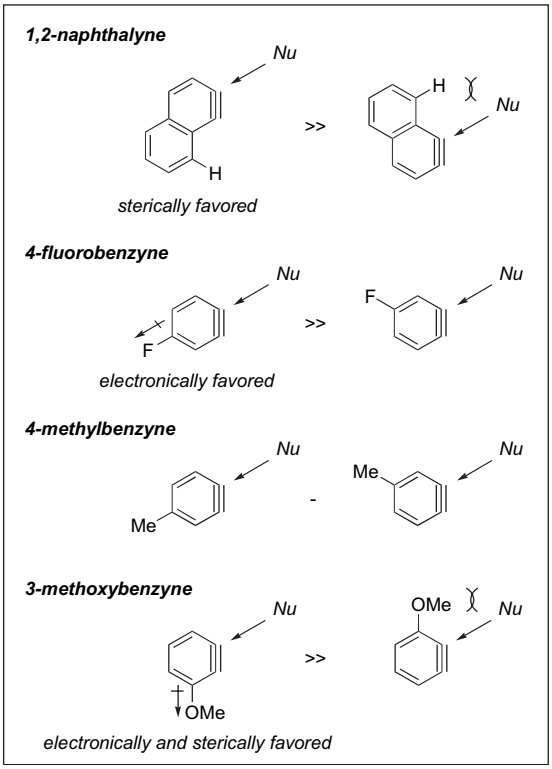
The three-component coupling would be commenced by a nucleophilic addition of an isocyanide to an aryne, as



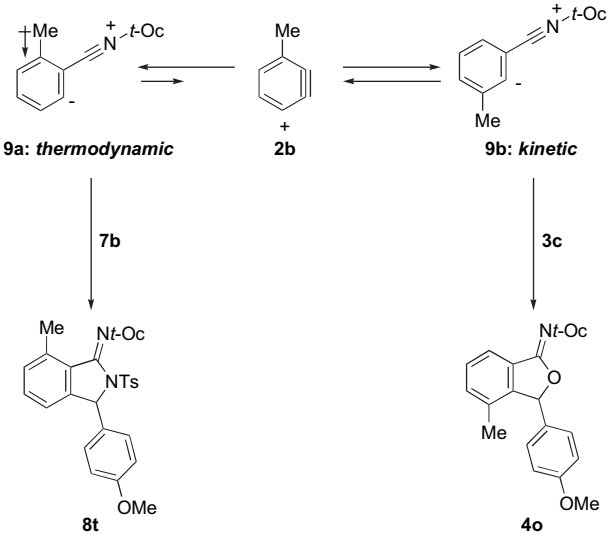
Scheme 8.

depicted in Scheme 9.[15] Subsequent nucleophilic attack of the resulting zwitterion (**9**) to an electrophile gives **10**, which then undergoes intramolecular cyclization to provide the product. The observed perfect regioselectivity in the reaction of 1,2-naphthalyne can be rationally explained by steric effect, which favors the nucleophilic attack at 2-position of the naphthalene ring with avoiding a steric repulsion between *peri* hydrogen and an incoming isocyanide. Owing to a strong electron-withdrawing effect of a fluoro substituent, the developing negative charge at the *meta* position (vs *para*) would be stabilized to a greater extent in the transition state for the addition of an isocyanide to 4-fluorobenzyne, which results in the regioselective formation of **4q**.[16] In contrast, steric and electronic effects around the triple bond would be negligible in the reaction of 4-methylbenzyne, and equal addition of an isocyanide to both ends of the triple bond occurs. Exclusive formation of **4p** or **8s** can be attributed to an electron-withdrawing inductive effect (−I effect) of a methoxy moiety together with a steric effect, both of which direct the nucleophilic attack toward the *meta* position of the methoxy moiety.[17] In the cases of 3-methylbenzyne, the different regioselectivities depended on electrophiles would be ascribable to reversibility in the nucleophilic addition of an isocyanide to 3-methylbenzyne (Scheme 10).[18] Thus, the zwitterion bearing the anionic moiety at the *meta* position of the methyl group (**9a**) would be thermodynamically stable among two possible zwitterions owing to an electron-donating character of the methyl group (+I effect). In contrast, formation of another zwitterion (**9b**) should be kinetically favored because of less steric repulsion between the methyl group and an incoming isocyanide. Therefore, a sulfonylimine of low reactivity toward **9** as compared with an aldehyde gave **8t** predominantly, since kinetically





Scheme 9.



Scheme 10.

generated zwitterion **9b** should isomerize to thermodynamically stable **9a** prior to the reaction with the sulfonylimine.[19] To the contrary, an aldehyde would readily react with **9b** to provide **4o** exclusively.

3. Conclusion

We have demonstrated that a variety of arynes, despite their transient nature, can be utilized in selective three-component coupling reactions by the use of isocyanides and suitable electrophiles. Based on the present reactions, benzoannulated iminodihydroisobenzofurans or iminoisoindolines of structural complexity and diversity, which are difficult to obtain by conventional methods, can be synthesized straightforwardly. In the reactions with 3-methylbenzyne, differences in reactivities of electrophiles have been found to govern regioselectivities, which demonstrates that nucleophilic addition of isocyanides to arynes, a first step of the reactions, is reversible.

4. Experimental

4.1. General

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz) spectrometer using residual chloroform (^{1}H), $CDCl_3$ (^{13}C), or THF-d_8 (^{13}C) as an internal standard. High-resolution mass spectra were obtained with a Hitachi M-80B spectrometer or a JEOL JMS-HX110A spectrometer. Melting points were measured with Yanaco Micro Melting Point apparatus and are uncorrected. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (benzene as an eluant). Column chromatography was carried out using Merck Aluminum oxide 90 active neutral or Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray dried) was vacuum dried at 100 °C for 12 h.

4.2. Aryne precursors

2-(Trimethylsilyl)phenyl triflate (**1a**),[11] 1-(trimethylsilyl)-2-naphthyl triflate (**1b**),[20] 2-(trimethylsilyl)-1-naphthyl triflate (**1c**),[5a] 6-methyl-2-(trimethylsilyl)phenyl triflate (**1d**),[21] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1e**),[22] 4-fluoro-2-(trimethylsilyl)phenyl triflate (**1f**),[8a,23] 4-methyl-2-(trimethylsilyl)phenyl triflate (**1g**),[24] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1h**),[25] 6-(trimethylsilyl)-5-indanyl triflate (**1i**),[25] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1j**),[25] 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (**1k**),[5b] 3-(trimethylsilyl)-2-naphthyl triflate (**1l**),[5b] and 3,6-dimethyl-2-(trimethylsilyl)phenyl triflate (**1m**)[5b] were prepared according to literature procedures.

4.3. Isocyanides

tert-Butyl isocyanide (**2a**), *tert*-octyl isocyanide (**2b**), cyclohexyl isocyanide (**2d**), and *n*-octyl isocyanide (**2e**) were synthesized from the corresponding amines by a literature method.[26] 1-Adamantyl isocyanide (**2c**) was prepared according to a literature procedure.[27]

4.4. Sulfonylimines

All sulfonylimines were prepared according to a literature method.[28]

4.5. Three-component coupling of arynes, isocyanides, and carbonyl compounds: a general procedure

To a THF solution (1.0 mL) of KF (0.035 g, 0.60 mmol), 18-crown-6 (0.16 g, 0.60 mmol), an isocyanide (0.15 mmol), and a carbonyl compound (0.30 mmol) was added an aryne precursor (0.30 mmol), and the resulting mixture was stirred at 0 °C. The mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Alumina column chromatography (25% ethyl acetate/hexane as an eluant, Activity III) followed by gel permeation chromatography gave the corresponding product.

4.5.1. *N*-(3-Phenyl-(3*H*)-isobenzofuranylidene)-*tert*-butylamine (4a). Isolated in 46% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9H), 6.39 (s, 1H), 7.13–7.17 (m, 1H), 7.26–7.42 (m, 7H), 7.86–7.90 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.52, 53.95, 85.49, 121.01, 122.72, 124.08, 127.14, 129.03, 129.33, 131.61, 132.67, 140.71, 146.99, 155.44. HRMS Calcd for $C_{17}H_{16}ON$: M^+-Me, 250.1231. Found: *m*/*z* 250.1238.

4.5.2. *N*-[3-(1-Naphthyl)-(3*H*)-isobenzofuranylidene]-*tert*-butylamine (4b). Isolated in 49% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9H), 7.18–7.24 (m, 2H), 7.35–7.46 (m, 4H), 7.52–7.62 (m, 2H), 7.84–7.94 (m, 3H), 8.16 (d, J=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 30.1, 53.8, 82.3, 122.1, 123.3, 123.8, 124.6, 125.4, 125.9, 126.6, 128.3, 128.7, 129.0, 129.2, 131.0, 131.9, 134.0, 134.4, 145.4, 156.1. HRMS Calcd for $C_{21}H_{18}NO$: M^+-Me, 300.1387. Found: *m*/*z* 300.1349.

4.5.3. *N*-[3-(4-Methoxyphenyl)-(3*H*)-isobenzofuranylidene]-*tert*-butylamine (4c). Isolated in 37% yield as a white powder: mp 86–89 °C; ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 9H), 3.80 (s, 3H), 6.34 (s, 1H), 6.88 (d, J=8.7 Hz, 2H), 7.11–7.13 (m, 1H), 7.18 (d, J=8.7 Hz, 2H), 7.37–7.44 (m, 2H), 7.83–7.85 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 30.03, 53.65, 55.27, 84.70, 114.11, 121.96, 123.50, 128.05, 128.43, 131.10, 131.19, 131.59, 145.96, 156.23, 159.82. HRMS: Calcd for $C_{19}H_{21}O_2N$: M^+, 295.1571. Found: *m*/*z* 295.1530.

4.5.4. *N*-(3-Phenyl-(3*H*)-isobenzofuranylidene)-*tert*-octylamine (4d). Isolated in 65% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.47 (s, 6H), 1.77 (s, 2H), 6.37 (s, 1H), 7.13–7.17 (m, 1H), 7.27–7.41 (m, 7H), 7.78–7.82 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.9, 32.4, 32.7, 56.2, 57.9, 85.6, 122.9, 124.2, 127.4, 129.2, 129.5, 129.7, 131.8, 133.0, 140.7, 147.1, 152.5. HRMS Calcd for $C_{22}H_{27}NO$: M^+, 321.2093. Found: *m*/*z* 321.2100.

4.5.5. *N*-[3-(1-Naphthyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4e). Isolated in 73% yield as a white powder: mp 96–100 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.48 (s, 6H), 1.78 (s, 2H), 7.19 (s, 1H), 7.23–7.25 (m, 1H), 7.36–7.45 (m, 4H), 7.53–7.64 (m, 2H), 7.84–7.94 (m, 3H), 8.19–8.22 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.9, 31.0, 32.4, 32.7, 56.3, 57.9, 82.9, 123.1, 124.4, 125.2, 126.0, 126.7, 127.3, 128.8, 129.3, 129.7, 129.9, 131.6, 132.2, 133.5, 135.2, 136.0, 146.6, 154.6. HRMS Calcd for $C_{26}H_{29}NO$: M^+, 371.2249. Found: *m*/*z* 371.2237.

4.5.6. *N*-[3-(4-Methoxyphenyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4f). Isolated in 73% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.44 (s, 6H), 1.75 (s, 2H), 3.80 (s, 3H), 6.33 (s, 1H), 6.88 (d, J=8.7 Hz, 2H), 7.11–7.14 (m, 1H), 7.19 (d, J=8.7 Hz, 2H), 7.38–7.41 (m, 2H), 7.77–7.81 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.86, 30.92, 32.4, 32.7, 55.4, 56.2, 57.8, 85.5, 114.8, 123.0, 124.1, 128.9, 129.1, 131.6, 132.5, 147.2, 161.1. HRMS Calcd for $C_{22}H_{26}NO_2$: M^+-Me, 336.1964. Found: *m*/*z* 336.1985.

4.5.7. *N*-[3-(4-Trifluoromethylphenyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4g). Isolated in 69% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.48 (s, 6H), 1.78 (s, 2H), 6.42 (s, 1H), 7.14–7.17 (m, 1H), 7.40–7.44 (m, 4H), 7.64 (d, J=8.5 Hz, 2H), 7.81–7.85 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.8, 31.0, 32.4, 32.8, 56.3, 58.0, 84.5, 122.9, 124.4, 124.5 (J_{C-F}=272.1 Hz), 126.4 (J_{C-F}=3.3 Hz), 127.8, 129.0, 129.6, 131.1 (J_{C-F}=32.8 Hz), 132.0, 132.7, 145.2, 154.2. HRMS Calcd for $C_{23}H_{26}F_3NO$: M^+-Me, 389.1966. Found: *m*/*z* 389.1974.

4.5.8. *N*-[3-(3-Methoxyphenyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4h). Isolated in 65% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.48 (s, 6H), 1.78 (s, 2H), 3.77 (s, 3H), 6.34 (s, 1H), 6.80–6.92 (m, 3H), 7.15–7.18 (m, 1H), 7.28–7.41 (m, 3H), 7.78–7.83 (m, 1H); ^{13}C NMR (THF-d_8) δ 30.8, 31.0, 32.4, 32.8, 55.4, 56.2, 57.9, 85.4, 112.7, 114.6, 119.2, 122.9, 124.1, 129.2, 130.4, 131.7, 132.8, 142.3, 147.0, 154.7, 161.1. HRMS Calcd for $C_{22}H_{26}NO_2$: M^+-Me, 336.1964. Found: *m*/*z* 336.1974.

4.5.9. *N*-[3-(2,4-Dimethylphenyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4i). Isolated in 61% yield as a white powder: mp 79–81 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.44 (s, 6H), 1.75 (s, 2H), 2.31 (s, 3H), 2.42 (s, 3H), 6.60 (s, 1H), 6.89–6.93 (m, 2H), 7.04 (s, 1H), 7.12–7.16 (m, 1H), 7.39–7.42 (m, 2H), 7.79–7.82 (m, 1H); ^{13}C NMR (THF-d_8) δ 19.3, 21.1, 30.8, 30.9, 32.4, 32.7, 56.2, 57.8, 83.5, 123.0, 124.2, 127.5, 128.2, 129.1, 131.6, 132.4, 133.8, 135.1, 137.1, 138.9, 146.5, 154.9. HRMS Calcd for $C_{24}H_{31}NO$: M^+, 349.2406. Found: *m*/*z* 349.2416.

4.5.10. *N*-[3-(2-Thienyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4j). Isolated in 50% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.44 (s, 3H), 1.45 (s, 3H), 1.71 (d, J=14.4 Hz, 1H), 1.82 (d, J=14.4 Hz, 1H), 6.64 (s, 1H), 7.00 (dd, J=4.9 Hz, 3.5 Hz, 1H), 7.12 (d, J=3.1 Hz, 1H), 7.28–7.32 (m, 2H), 7.41–7.49 (m, 2H), 7.81 (d, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 30.40, 30.44, 31.8, 32.0, 54.8, 57.5, 80.0, 122.1, 123.7, 126.0, 126.5, 126.7, 128.9, 131.0, 131.9, 142.5, 144.7, 153.5. HRMS Calcd for $C_{20}H_{25}NOS$: M^+, 327.1657. Found: *m*/*z* 327.1630.

4.5.11. *N*-(3-Ethyl-(3*H*)-isobenzofuranylidene)-*tert*-octylamine (4k). Isolated in 50% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J=8.0 Hz, 3H), 1.06 (s, 9H), 1.41 (s, 6H), 1.70–1.77 (m, 3H), 2.00–2.10 (m, 1H), 5.41 (dd, J=6.8, 4.1 Hz, 1H), 7.26 (d, J=7.2 Hz, 1H), 7.35–7.39 (m, 1H), 7.42–7.46 (m, 1H), 7.74 (d, J=7.5 Hz, 1H); ^{13}C NMR (THF-d_8) δ 9.4, 29.5, 30.85, 30.94, 32.4, 32.7, 56.2, 57.7, 84.8, 121.9, 124.1, 129.0, 131.4, 134.0, 146.6, 154.9. HRMS Calcd for $C_{18}H_{27}NO$: M^+, 273.2093. Found: *m*/*z* 273.2088.

4.5.12. *N*-(3-*tert*-Butyl-(3*H*)-isobenzofuranylidene)-*tert*-octylamine (4l). Isolated in 40% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.03 (s, 9H), 1.45 (s, 3H), 1.47 (s, 3H), 1.70 (d, J=14.4 Hz, 1H), 1.80 (d, J=14.4 Hz, 1H), 5.11 (s, 1H), 7.36–7.43 (m, 3H), 7.75 (d, J=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 29.9, 30.3, 31.9, 32.0, 36.2, 55.2, 57.1, 90.6, 122.6, 123.5, 128.2, 130.1, 133.8, 143.6, 154.8. HRMS Calcd for $C_{20}H_{31}NO$: M^+, 301.2406. Found: *m*/*z* 301.2423.

4.5.13. *N*-[3-(4-Methoxyphenyl)-(3*H*)-isobenzofuranylidene]-1-adamantylamine (4m). Isolated in 77% yield as a white powder: mp 122–126 °C; ^{1}H NMR ($CDCl_3$) δ 1.50–1.61 (m, 6H), 1.97 (s, 9H), 3.70 (s, 3H), 6.22 (s, 1H), 6.79 (d, J=8.7 Hz, 2H), 7.00–7.02 (m, 1H), 7.07 (d, J=8.7 Hz, 2H), 7.28–7.32 (m, 2H), 7.74–7.76 (m, 1H); ^{13}C NMR (THF-d_8) δ 31.0, 37.7, 43.7, 54.8, 55.4, 85.5, 114.8, 122.9, 124.2, 128.8, 129.0, 131.7, 132.6, 133.0, 147.4, 155.5, 161.0. HRMS Calcd for $C_{25}H_{27}NO_2$: M^+, 373.2042. Found: *m*/*z* 373.2004.

4.5.14. *N*-[3-(4-Methoxyphenyl)-(3*H*)-benzo[*e*]isobenzofuranylidene]-1-*tert*-octylamine (4n). Isolated in 40% (from **1b**) or 41% (from **1c**) yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9H), 1.54 (s, 6H), 1.88 (s, 2H), 3.81 (s, 3H), 6.38 (s, 1H), 6.89 (d, J=8.6 Hz, 2H), 7.18 (d, J=8.6 Hz, 1H), 7.23 (d, J=8.6 Hz, 2H), 7.56 (t, J=6.8 Hz, 1H), 7.68 (t, J=8.4 Hz, 1H), 7.85–7.90 (m, 2H), 9.59 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 30.7, 30.8, 32.0, 32.1, 54.9, 55.3, 57.9, 83.9, 114.1, 119.2, 125.0, 125.4, 126.4, 127.9, 128.1, 128.4, 129.0, 131.3, 132.0, 133.5, 145.9, 154.9, 159.9. HRMS Calcd for $C_{27}H_{31}NO_2$: M^+, 401.2355. Found: *m*/*z* 401.2325.

4.5.15. *N*-[3-(4-Methoxyphenyl)-4-methyl-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4o). Isolated in 45% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.43 (s, 3H), 1.44 (s, 3H), 1.74 (d, J=14.2 Hz, 1H), 1.79 (d, J=14.2 Hz, 1H), 2.73 (s, 3H), 3.80 (s, 3H), 6.24 (s, 1H), 6.87–6.93 (m, 3H), 7.14–7.26 (m, 4H); ^{13}C NMR (THF-d_8) δ 18.5, 30.5, 30.7, 31.9, 32.0, 54.9, 55.3, 57.6, 83.4, 114.0, 119.3, 128.1, 128.9, 130.1, 130.4, 132.1, 137.4, 146.5, 154.3, 159.6. HRMS Calcd for $C_{24}H_{31}NO_2$: M^+, 350.2120. Found: *m*/*z* 350.2075.

4.5.16. *N*-[3-(4-Methoxyphenyl)-4-methoxy-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4p). Isolated in 16% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 9H), 1.42 (s, 6H), 1.73 (s, 2H), 3.70 (s, 3H), 3.80 (s, 3H), 6.36 (s, 1H), 6.82–6.87 (m, 3H), 7.19 (d, J=8.6 Hz, 2H), 7.36–7.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 30.1, 30.4, 31.8, 32.0, 54.8, 55.2, 55.5, 57.3, 83.4, 112.3, 113.6, 115.4, 128.5, 130.4, 130.8, 133.5, 154.3, 154.6, 159.5. HRMS Calcd for $C_{24}H_{31}NO_3$: M^+, 381.2304. Found: *m*/*z* 381.2358.

4.5.17. *N*-[3-(4-Methoxyphenyl)-5-fluoro-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4q). Isolated in 38% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.44 (s, 6H), 1.77 (s, 2H), 3.81 (s, 3H), 6.29 (s, 1H), 6.80 (dd, J=2.2 Hz, J_{H-F}=8.1 Hz, 1H), 6.90 (d, J=8.6 Hz, 2H), 7.08 (td, J=8.9, 2.2 Hz, 1H), 7.17 (d, J=8.6 Hz, 2H), 7.64–7.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 30.3, 30.4, 31.8, 32.0, 55.0, 55.3, 57.5, 83.9, 109.1 (J_{C-F}=24.4 Hz), 114.16, 114.23, 116.4 (J_{C-F}=23.1 Hz), 125.5 (J_{C-F}=9.8 Hz), 128.1, 130.7, 148.1 (J_{C-F}=9.8 Hz), 153.3, 160.0, 164.8 (J_{C-F}= 251.0 Hz). HRMS Calcd for $C_{23}H_{28}FNO_2$: M^+, 369.2104. Found: *m*/*z* 369.2076.

4.5.18. A mixture of *N*-[3-(4-methoxyphenyl)-6-methyl-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4r) and *N*-[3-(4-methoxyphenyl)-5-methyl-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4′r). Isolated in 58% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 18H), 1.44 (s, 12H), 1.76–1.77 (m, 4H), 2.35 (s, 3H), 2.40 (s, 3H), 3.798 (s, 3H), 3.804 (s, 3H), 6.27 (s, 1H), 6.29 (s, 1H), 6.86–6.91 (m, 5H), 7.00 (d, J=7.8 Hz, 1H), 7.17–7.25 (s, 6H), 7.60 (s, 1H), 7.67 (d, J=7.8 Hz, 1H); ^{13}C NMR (THF-d_8) δ 21.2, 21.6, 30.96, 31.00, 31.03, 31.07, 32.4, 32.7, 55.4, 56.0, 56.1, 57.7, 57.8, 85.25, 85.35, 114.69, 114.71, 122.7, 123.2, 123.8, 124.1, 128.9, 130.1, 130.7, 132.7, 133.5, 139.1, 142.16, 144.6, 147.6, 154.7, 154.8, 161.0. HRMS Calcd for $C_{24}H_{31}NO_2$: M^+, 365.2355. Found: *m*/*z* 365.2365.

4.5.19. *N*-[3-(4-Methoxyphenyl)-5,6-dimethyl-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4s). Isolated in 61% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.44 (s, 6H), 1.76 (d, J=14.5 Hz, 1H), 1.80 (s, J=14.5 Hz, 1H), 2.25 (s, 3H), 2.30 (s, 3H), 3.80 (s, 3H), 6.26 (s, 1H), 6.86–6.91 (m, 3H), 7.18 (d, J=8.7 Hz, 2H), 7.57 (s, 1H); ^{13}C NMR (THF-d_8) δ 19.7, 20.3, 30.5, 30.6, 31.9, 32.0, 54.5, 55.2, 57.2, 84.2, 114.0, 122.7, 123.9, 128.1, 129.8, 131.8, 137.3, 140.3, 143.9, 155.0, 159.7. HRMS Calcd for $C_{25}H_{33}NO_2$: M^+, 379.2511. Found: *m*/*z* 379.2516.

4.5.20. *N*-[3-(4-Methoxyphenyl)-5,6-propylen-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4t). Isolated in 31% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.45 (s, 6H), 1.78 (s, 2H), 2.09 (quintet, J=7.24 Hz, 2H), 2.85 (dd, J=14.4, 7.1 Hz, 2H), 2.92 (t, J=7.2 Hz, 2H), 3.80 (s, 3H), 6.27 (s, 1H), 6.89 (d, J=8.7 Hz, 2H), 6.93 (s, 1H), 7.20 (d, J=8.7 Hz, 2H), 7.64 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.8, 30.4, 30.6, 31.9, 32.0, 32.2, 32.7, 54.7, 55.2, 57.2, 84.3, 114.0, 117.5, 118.9, 128.3, 130.3, 131.8, 144.7, 145.3, 148.4, 155.1, 159.7. HRMS Calcd for $C_{26}H_{33}NO_2$: M^+, 391.2511. Found: *m*/*z* 391.2522.

4.5.21. *N*-[3-(4-Methoxyphenyl)-4,7-dimethoxy-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (4u). Isolated in 26% yield as a white powder: mp 122–126 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 9H), 1.42 (s, 3H), 1.44 (s, 3H), 1.66 (d, J=14.2 Hz, 1H), 1.73 (d, J=14.2 Hz, 1H), 3.61 (s, 3H), 3.79 (s, 3H), 3.87 (s, 3H), 6.27 (s, 1H), 6.79 (s, 2H), 6.83 (d, J=8.9 Hz, 2H), 7.19 (d, J=8.9 Hz, 2H); ^{13}C NMR (THF-d_8) δ 29.3, 29.6, 31.8, 32.0, 55.2, 55.9, 56.3, 57.7, 82.3, 112.1, 113.5, 113.8, 120.9, 128.4, 131.0, 136.2,

147.9, 150.7, 153.3, 159.3. HRMS Calcd for $C_{25}H_{33}NO_4$: M^+, 411.2410. Found: *m/z* 411.2430.

4.5.22. *N*-(3-Methyl-3-phenyl-(3*H*)-isobenzofuranylidene)-*tert*-octylamine (6a). Isolated in 18% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 9H), 1.49 (s, 3H), 1.50 (s, 3H), 1.77 (d, J=14.4 Hz, 1H), 1.86 (d, J=14.4 Hz, 1H), 1.99 (s, 3H), 7.25–7.46 (m, 8H), 7.78 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 27.7, 30.3, 30.5, 31.9, 32.0, 54.7, 57.4, 114.4, 121.3, 123.8, 125.1, 127.0, 127.7, 128.1, 128.5, 129.5, 149.9. HRMS Calcd for $C_{23}H_{29}NO$: M^+, 335.2249. Found: *m/z* 335.2241.

4.5.23. *N*-[3-(4-Chlorophenyl)-3-methyl-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6b). Isolated in 33% yield as a yellow solid: mp 49–52 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.48 (s, 3H), 1.49 (s, 3H), 1.75 (d, J=14.2 Hz, 1H), 1.86 (d, J=14.2 Hz, 1H), 1.95 (s, 3H), 7.22–7.24 (m, 1H), 7.31 (d, J=8.9 Hz, 2H), 7.36–7.45 (m, 4H), 7.77 (br d, J=6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.7, 30.3, 30.5, 31.9, 32.0, 54.8, 57.4, 88.2, 121.2, 123.9, 126.6, 128.6, 131.0, 131.4, 133.6, 141.8, 149.3, 153.2. HRMS Calcd for $C_{22}H_{25}ClNO$: M^+−Me, 354.1623. Found: *m/z* 354.1589.

4.5.24. *N*-{3-Methyl-3-[4-(trifluoromethyl)phenyl]-(3*H*)-isobenzofuranylidene}-*tert*-octylamine (6c). Isolated in 25% yield as a yellow oil: ^{1}H NMR (THF-d_8) δ 1.08 (s, 9H), 1.50 (s, 3H), 1.52 (s, 3H), 1.76 (d, J=14.2 Hz, 1H), 1.88 (d, J=14.2 Hz, 1H), 2.02 (s, 3H), 7.38–7.49 (m, 3H), 7.67–7.76 (m, 5H); ^{13}C NMR (THF-d_8) δ 27.9, 30.8, 31.1, 32.4, 32.7, 56.2, 58.0, 89.3, 122.4, 124.5, 126.1 (J_{C-F}= 271.6 Hz), 126.3 (J_{C-F}=4.1 Hz), 126.6, 129.5, 130.4 (J_{C-F}= 32.0 Hz), 132.0, 132.3, 148.9, 150.2, 153.4. HRMS Calcd for $C_{24}H_{28}F_3NO$: M^+, 403.2123. Found: *m/z* 403.2107.

4.5.25. *N*-[3-Phenyl-3-(trifluoromethyl)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6d). Isolated in 42% yield as a white solid: mp 72–74 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.54 (s, 3H), 1.55 (s, 3H), 1.82 (d, J=14.4 Hz, 1H), 1.87 (d, J=14.4 Hz, 1H), 7.39–7.45 (m, 3H), 7.50–7.58 (m, 2H), 7.70–7.76 (m, 3H), 7.82 (br d, J=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 30.42, 30.43, 31.8, 32.1, 55.1, 57.9, 87.5 (J_{C-F}=31.1 Hz), 123.4, 123.8 (J_{C-F}=284.3 Hz), 124.2, 126.4, 128.6, 129.3, 130.2, 131.3, 132.7, 134.5, 140.5, 150.6. HRMS Calcd for $C_{22}H_{23}F_3NO$: M^+, 374.1730. Found: *m/z* 374.1722.

4.5.26. *N*-(3-Benzoyl-3-phenyl-(3*H*)-isobenzofuranylidene)-*tert*-octylamine (6e). Isolated in 20% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9H), 1.38 (s, 3H), 1.48 (s, 3H), 1.56 (d, J=14.4 Hz, 1H), 1.70 (d, J=14.4 Hz, 1H), 1.99 (s, 3H), 7.31–7.64 (m, 11H), 7.74 (br s, 1H), 7.92 (d, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 30.1, 30.7, 31.6, 31.8, 54.5, 57.5, 94.7, 124.1, 125.0, 128.1, 128.5, 129.0, 129.3, 130.2, 130.7, 131.1, 133.1, 134.8, 139.7, 144.9, 151.9, 195.1. HRMS Calcd for $C_{28}H_{28}NO_2$: M^+, 410.2119. Found: *m/z* 410.2098.

4.5.27. *N*-[3,3-(3-Oxo-penta-1,4-dienylene)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6f). Isolated in 32% yield as an orange solid: mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 9H), 1.44 (s, 6H), 1.76 (s, 2H), 6.33 (d, J=10.2 Hz, 2H), 6.68 (d, J=10.2 Hz, 2H), 7.10–7.12 (m, 1H), 7.46–7.48 (m, 2H), 7.80 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 30.4, 31.8, 32.0, 54.9, 57.9, 82.1, 121.7, 124.7, 128.5, 128.9, 131.6, 132.6, 142.0, 146.4, 151.7, 184.9. HRMS Calcd for $C_{20}H_{22}NO_2$: M^+, 308.1649. Found: *m/z* 308.1631.

4.5.28. *N*-[3,3-(1,4-Di-*tert*-butyl-3-oxo-penta-1,4-dienylene)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6g). Isolated in 51% yield as a pale yellow solid: mp 125–128 °C; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.06 (s, 9H), 1.16 (s, 9H), 1.48 (s, 3H), 1.51 (s, 3H), 1.67 (d, J=14.5 Hz, 1H), 1.91 (d, J=14.5 Hz, 1H), 6.13 (s, 1H), 6.38 (s, 1H), 6.95–6.99 (m, 1H), 7.39–7.42 (m, 2H), 7.74 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.8, 30.45, 30.50, 30.7, 31.9, 32.0, 34.0, 37.1, 55.4, 57.7, 87.4, 120.8, 124.5, 128.7, 129.2, 131.4, 133.0, 142.5, 144.5, 144.6, 152.1, 163.2, 186.7. HRMS Calcd for $C_{29}H_{41}NO_2$: M^+, 435.3137. Found: *m/z* 435.3152.

4.5.29. *N*-[3,3-(2,4-Di-*tert*-butyl-3-oxo-penta-1,4-dienylene)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6h). Isolated in 41% yield as a yellow solid: mp 100–103 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 9H), 1.24 (s, 18H), 1.47 (s, 6H), 1.83 (s, 2H), 6.38 (s, 2H), 6.95–6.97 (m, 1H), 7.39–7.45 (m, 2H), 7.80 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.3, 30.5, 31.9, 32.0, 35.0, 54.5, 57.7, 83.6, 121.2, 124.4, 129.2, 131.5, 132.7, 138.2, 143.8, 147.1, 152.7, 186.4. HRMS Calcd for $C_{29}H_{41}NO_2$: M^+, 435.3137. Found: *m/z* 435.3138.

4.5.30. *N*-[3,3-(1,5-Di-*tert*-butyl-3-oxo-penta-1,4-dienylene)-(3*H*)-isobenzofuranylidene]-*tert*-octylamine (6′h). Isolated in 11% yield as an orange oil: ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 27H), 1.58 (s, 6H), 1. 70 (s, 2H), 6.28 (s, 2H), 6.99 (dd, J=6.2, 1.8 Hz, 1H), 7.31–7.38 (m, 2H), 7.60–7.62 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 30.0, 31.0, 31.8, 32.1, 38.6, 57.7, 57.9, 94.1, 121.4, 123.1, 131.3, 133.8, 145.4, 151.0, 172.6, 188.0. HRMS Calcd for $C_{29}H_{41}NO_2$: M^+, 435.3137. Found: *m/z* 435.3152.

4.6. Three-component coupling using 3j or 3k

To a THF solution (2.5 mL) of KF (0.087 g, 1.5 mmol), 18-crown-6 (0.40 g, 1.5 mmol), **2b** (0.052 g, 0.38 mmol), and **3j** (or **3k**) (0.020 g, 0.15 mmol) was added **1a** (0.22 g, 0.75 mmol), and the resulting mixture was stirred at 0 °C for 7 h. The mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Alumina column chromatography (25% ethyl acetate/hexane as an eluant, Activity III) followed by gel permeation chromatography gave the corresponding product.

4.6.1. 1,4-Bis(1-*tert*-octylimino-1,3-dihydro-3-isobenzofuranyl)benzene (a mixture of diastereomers) (4v). Isolated in 38% yield as a yellow powder: mp 147–151 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 18H), 1.458 (s, 6H), 1.464 (s, 6H), 1.76 (s, 4H), 6.36 (s, 1H), 6.37 (s, 1H), 7.13–7.15 (m, 2H), 7.30 (d, J=3.6 Hz, 4H), 7.39–7.41 (m, 4H), 7.79–7.81 (m, 2H); ^{13}C NMR (THF-d_8) δ 30.27, 30.32, 30.4, 31.9, 32.0, 54.9, 55.0, 57.4, 84.1, 84.2, 121.9, 123.6, 126.8, 126.9, 128.3, 128.6, 130.9, 131.8, 131.9, 139.8, 145.3, 145.4, 154.0. HRMS Calcd for $C_{37}H_{45}N_2O_2$: M^+−Me, 549.3479. Found: *m/z* 549.3519.

4.6.2. 1,3-Bis(1-*tert*-octylimino-1,3-dihydro-3-isobenzofuranyl)benzene (a mixture of diastereomers) (4w). Isolated in 35% yield as a white powder: mp 71–74 °C; ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 18H, *minor*), 1.04 (s, 18H, *major*), 1.39–1.41 (m, 12H, *minor*), 1.47–1.48 (m, 12H, *major*), 1.75 (br s, 4H, *minor*), 1.77 (br s, 4H, *major*), 6.34 (br s, 2H), 7.08–7.15 (m, 2H), 7.24–7.25 (m, 3H), 7.34–7.42 (m, 7H), 7.81–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 30.2, 30.3, 30.4, 31.8, 31.9, 31.995, 32.044, 55.0, 55.1, 57.4, 57.5, 84.3, 121.9, 123.7, 124.5, 124.8, 126.5, 126.8, 128.3, 128.7, 129.2, 129.3, 131.76, 131.84, 140.07, 141.12, 145.26, 145.34, 152.3, 154.2. Anal. Calcd for $C_{38}H_{48}N_2O_2$: C, 80.81; H, 8.57; N, 4.96. Found: C, 80.59; H, 8.28; N, 5.21.

4.7. Three-component coupling of arynes, isocyanides, and sulfonylimines: a general procedure

To a THF solution (2.0 mL) of KF (0.070 g, 1.20 mmol), 18-crown-6 (0.32 g, 1.20 mmol), an isocyanide (0.30 mmol) and a sulfonylimine (0.60 mmol) was added an aryne precursor (0.60 mmol), and the resulting mixture was stirred at room temperature. The mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Silica gel column chromatography (17% ethyl acetate/hexane as an eluant) followed by gel permeation chromatography gave the corresponding product.

4.7.1. *N*-(3-Phenyl-2-tosylisoindolinylidene)-*tert*-octylamine (8a). Isolated in 64% yield as a colorless needle: mp 131–133 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.48 (s, 6H), 1.75 (d, J=14.5 Hz, 1H), 2.03 (d, J=14.5 Hz, 1H), 2.36 (s, 3H), 6.28 (s, 1H), 7.10 (d, J=8.2 Hz, 2H), 7.12–7.15 (m, 1H), 7.23–7.25 (m, 2H), 7.32–7.41 (m, 5H), 7.48 (d, J=8.2 Hz, 2H), 8.01–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.3, 31.6, 31.8, 53.4, 57.8, 64.1, 124.6, 127.5, 127.7, 127.9, 128.2, 128.3, 128.5, 128.8, 130.9, 137.7, 140.7, 142.9, 146.4, 146.7. Anal. Calcd for $C_{29}H_{34}N_2O_2S$: C, 73.38; H, 7.22; N, 5.90. Found: C, 73.51; H, 7.19; N, 5.84.

4.7.2. *N*-[3-(4-Methoxyphenyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8b). Isolated in 61% yield as a pale yellow solid: mp 144–146 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9H), 1.45 (s, 3H), 1.46 (s, 3H), 1.72 (d, J=14.5 Hz, 1H), 2.02 (d, J=14.5 Hz, 1H), 2.35 (s, 3H), 3.82 (s, 3H), 6.25 (s, 1H), 6.86 (d, J=8.2 Hz, 2H), 7.09–7.15 (m, 5H), 7.36–7.41 (m, 2H), 7.47 (d, J=7.5 Hz, 2H), 8.00–8.02 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.3, 31.6, 31.8, 31.9, 53.4, 55.2, 57.7, 63.6, 113.9, 124.6, 127.5, 127.6, 128.2, 128.3, 128.8, 129.0, 130.9, 132.8, 137.8, 142.8, 146.3, 147.0, 159.3. Anal. Calcd for $C_{30}H_{36}N_2O_3S$: C, 71.40; H, 7.19; N, 5.55. Found: C, 71.52; H, 7.14; N, 5.47.

4.7.3. *N*-{3-[4-(Trifluoromethyl)phenyl]-2-tosylisoindolinylidene}-*tert*-octylamine (8c). Isolated in 44% yield as a colorless solid: mp 142–144 °C; ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 1.46 (s, 3H), 1.47 (s, 3H), 1.74 (d, J=14.5 Hz, 1H), 2.02 (d, J=14.5 Hz, 1H), 2.37 (s, 3H), 6.32 (s, 1H), 7.10–7.14 (m, 3H), 7.37–7.43 (m, 4H), 7.51 (d, J=8.2 Hz, 2H), 7.60 (d, J=8.2 Hz, 2H), 8.02–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.2, 31.6, 31.9, 53.4, 57.9, 63.6, 124.0 (J_{C-F}=271.3 Hz), 124.5, 125.6 (J_{C-F}=4.1 Hz), 127.5, 127.8, 128.1, 128.3, 128.4, 128.7, 130.2 (J_{C-F}=31.7 Hz), 131.2, 137.4, 143.3, 145.0, 145.8, 146.1. Anal. Calcd for $C_{30}H_{33}F_3N_2O_2S$: C, 66.40; H, 6.13; N, 5.16. Found: C, 66.50; H, 6.19; N, 5.15.

4.7.4. *N*-[3-(2,4-Dimethylphenyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8d). Isolated in 66% yield as a colorless solid: mp 150–153 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.46 (s, 3H), 1.48 (s, 3H), 1.78 (d, J=14.5 Hz, 1H), 1.99 (d, J=14.5 Hz, 1H), 2.32 (s, 3H), 2.37 (s, 3H), 2.53 (br s, 3H), 6.53 (br s, 1H), 6.74 (br s, 1H), 6.88 (br s, 1H), 7.03 (br s, 1H), 7.06–7.12 (m, 3H), 7.34–7.38 (m, 2H), 7.50 (d, J=8.4 Hz, 2H). 7.99–8.02 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 19.3, 21.0, 21.4, 31.4, 31.6, 31.9, 53.6, 57.8, 59.9, 124.2, 126.9, 127.5, 127.7, 128.1, 128.9, 131.0, 131.7, 135.7, 137.2, 137.7, 142.8, 146.7, 147.2. Anal. Calcd for $C_{31}H_{38}N_2O_2S$: C, 74.06; H, 7.62; N, 5.57. Found: C, 74.05; H, 7.69; N, 5.36.

4.7.5. *N*-[3-(2,4,6-Trimethylphenyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8e). Isolated in 68% yield as a white solid: mp 147–149 °C; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 1.428 (s, 3H), 1.435 (s, 3H), 1.52 (s, 3H), 1.90 (s, 2H), 2.30 (s, 3H), 2.38 (s, 3H), 2.75 (s, 3H), 6.65 (s, 1H), 6.79 (s, 1H), 7.00 (s, 1H), 7.06–7.08 (m, 1H), 7.13 (d, J=8.4 Hz, 2H), 7.35–7.40 (m, 2H), 7.54 (d, J=8.4 Hz, 2H), 7.99–8.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.7, 20.9, 21.0, 31.5, 30.7, 31.7, 31.8, 54.0, 57.9, 59.9, 123.7, 127.3, 127.4, 128.1, 128.7, 128.8, 129.5, 130.9, 131.1, 132.8, 137.0, 137.27, 137.28, 137.8, 142.8, 145.5, 147.2. Anal. Calcd for $C_{32}H_{40}N_2O_2S$: C, 74.38; H, 7.80; N, 5.42. Found: C, 74.17; H, 8.06; N, 5.28.

4.7.6. *N*-[3-(1-Naphthyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8f). Isolated in 59% yield as a pale orange solid: mp 145–149 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 9H), 1.53 (s, 6H), 1.82 (d, J=14.8 Hz, 1H), 2.08 (d, J=14.8 Hz, 1H), 2.35 (s, 3H), 7.12–7.53 (m, 12H), 7.82 (d, J=8.0 Hz, 1H), 7.91 (d, J=7.5 Hz, 1H), 8.06 (d, J=8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.3, 31.6, 31.8, 31.9, 53.6, 57.9, 59.2, 114.3, 123.1, 123.9, 125.3, 125.6, 125.9, 126.4, 127.1, 127.7, 127.9, 128.1, 128.9, 130.8, 130.9, 134.1, 137.4, 142.9, 146.8, 147.2. Anal. Calcd for $C_{33}H_{36}N_2O_2S$: C, 75.54; H, 6.92; N, 5.34. Found: C, 75.53; H, 6.91; N, 5.38.

4.7.7. *N*-[3-(2-Thienyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8g). Isolated in 64% yield as a pale yellow needle: mp 142–144 °C; ^{1}H NMR ($CDCl_3$) δ 0.79, (s, 9H), 1.437 (s, 3H), 1.444 (s, 3H), 1.67 (d, J=14.5 Hz, 1H), 2.03 (d, J=14.5 Hz, 1H), 2.34 (s, 3H), 6.62 (s, 1H), 6.99–7.01 (m, 1H), 7.11 (d, J=8.2 Hz, 2H), 7.23–7.30 (m, 3H), 7.40–7.45 (m, 2H), 7.48 (d, J=8.2 Hz, 2H), 7.99–8.01 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.3, 31.6, 31.8, 32.0, 53.3, 57.8, 59.1, 124.7, 125.8, 126.5, 127.4, 127.6, 127.7, 128.1, 128.3, 128.6, 130.9, 137.7, 142.8, 144.3, 145.5, 146.0. Anal. Calcd for $C_{27}H_{32}N_2O_2S_2$: C, 67.46; H, 6.71; N, 5.83. Found: C, 67.66; H, 6.74; N, 5.80.

4.7.8. *N*-(3-Phenyl-2-tosylisoindolinylidene)-*tert*-butylamine (8h). Isolated in 55% yield as a white solid: mp 165–167 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 9H), 2.36 (s, 3H), 6.26 (s, 1H), 7.11 (d, J=8.2 Hz, 2H), 7.14–7.16 (m, 1H), 7.23–7.25 (m, 2H), 7.29–7.32 (m, 3H), 7.36–7.39 (m, 2H), 7.55 (d, J=8.2 Hz, 2H), 7.97–7.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 30.4, 53.5, 64.6, 124.5, 127.0,

127.4, 127.7, 127.87, 127.92, 128.2, 128.6, 128.9, 131.0, 137.3, 140.6, 143.0, 146.6, 147.4. Anal. Calcd for $C_{27}H_{32}N_2O_2S_2$: C, 71.74; H, 6.26; N, 6.69. Found: C, 71.67; H, 622; N, 6.72.

4.7.9. *N*-(3-Phenyl-2-tosylisoindolinylidene)-1-adamantylamine (8i). Isolated in 35% yield as a colorless needle: mp 174–178 °C; ^{1}H NMR ($CDCl_3$) δ 1.75 (br s, 6H), 2.06 (br s, 6H), 2.16 (br s, 3H), 2.37 (s, 3H), 6.25 (s, 1H), 7.09–7.14 (m, 3H), 7.21–7.25 (m, 2H), 7.29–7.33 (m, 3H), 7.36–7.40 (m, 2H), 7.51 (d, J=8.2 Hz, 2H), 8.08–8.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 29.7, 36.5, 42.2, 54.5, 64.4, 124.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.3, 128.5, 128.9, 130.9, 137.3, 140.6, 142.9, 146.6, 146.8. Anal. Calcd for $C_{32}H_{33}N_2O_2S$: C, 74.97; H, 6.49; N, 5.64. Found: C, 74.49; H, 6.52; N, 5.75.

4.7.10. *N*-(3-Phenyl-2-tosylisoindolinylidene)cyclohexylamine (8j). Isolated in 23% yield as a colorless needle: mp 163–165 °C; ^{1}H NMR ($CDCl_3$) δ 1.32–1.44 (m, 3H), 1.51–1.57 (m, 2H), 1.65–1.68 (m, 1H), 1.82–1.84 (m, 4H), 2.36 (s, 3H), 4.06–4.11 (m, 1H), 6.25 (s, 1H), 7.08–7.13 (m, 3H), 7.17–7.19 (m, 2H), 7.27–7.30 (m, 3H), 7.34–7.38 (m, 2H), 7.58 (d, J=8.2 Hz, 2H), 7.80 (d, J=7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 24.7, 25.8, 34.1, 34.5, 56.7, 65.9, 114.4, 124.4, 126.2, 127.6, 127.7, 128.0, 128.2, 128.3, 128.6, 128.8, 129.1, 129.3, 131.3, 136.8, 140.3, 143.2, 145.3. Anal. Calcd for $C_{27}H_{28}N_2O_2S$: C, 72.94; H, 6.35; N, 6.30. Found: C, 73.12; H, 6.53; N, 6.05.

4.7.11. *N*-(3-Phenyl-2-tosylisoindolinylidene)-*n*-octylamine (8k). Isolated in 46% yield as a white solid: mp 140–141 °C; ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J=6.8 Hz, 3H), 1.31–1.36 (m, 10H), 1.73 (quintet, J=7.1 Hz, 2H), 2.36 (s, 3H), 3.81–3.88 (m, 2H), 6.29 (s, 1H), 7.08–7.15 (m, 3H), 7.18–7.21 (m, 2H), 7.27–7.30 (m, 3H), 7.34–7.42 (m, 2H), 7.54 (d, J=8.2 Hz, 2H), 7.92 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.5, 22.7, 27.5, 29.4, 29.6, 31.9, 32.0, 49.8, 66.1, 114.4, 124.3, 126.5, 127.6, 128.0, 128.1, 128.3, 128.5, 128.9, 131.4, 136.8, 140.0. 143.3, 145.1, 150.7. Anal. Calcd for $C_{29}H_{34}N_2O_2S$: C, 73.38; H, 7.22; N, 5.90. Found: C, 73.50; H, 7.27; N, 5.95.

4.7.12. *N*-[3-(4-Methoxyphenyl)-5,6-dimethyl-2-tosylisoindolinylidene]-*tert*-octylamine (8l). Isolated in 78% yield as a white solid: mp 154–156 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.45 (s, 6H), 1.72 (d, J=14.4 Hz, 1H), 2.00 (d, J=14.4 Hz, 1H), 2.21 (s, 3H), 2.31 (s, 3H), 2.35 (s, 3H), 3.81 (s, 3H), 6.18 (s, 1H), 6.85–6.88 (m, 3H), 7.10 (d, J=7.5 Hz, 2H), 7.16 (d, J=7.5 Hz, 2H), 7.47 (d, J=6.8 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.0, 20.2, 21.4, 31.2, 31.5, 31.6, 31.8, 53.1, 55.15, 55.18, 57.5, 63.4, 113.7, 125.0, 125.3, 128.1, 128.2, 128.7, 128.9, 133.2, 136.2, 137.9, 140.5, 142.6, 144.9, 146.7, 159.1. Anal. Calcd for $C_{32}H_{40}N_2O_3S$: C, 72.14; H, 7.57; N, 5.26. Found: C, 72.15; H, 7.50; N, 5.10.

4.7.13. *N*-[3-(4-Methoxyphenyl)-2-tosyl-cyclopentano-[*f*]isoindolinylidene]-*tert*-octylamine (8m). Isolated in 75% yield as a white solid: mp 145–150 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9H), 1.43 (s, 6H), 1.70 (d, J=14.2 Hz, 1H), 1.99 (d, J=14.2 Hz, 1H), 2.08 (quintet, J=7.2 Hz, 2H), 2.35 (s, 3H), 2.80 (t, J=7.2 Hz, 1H), 2.86 (t, J=7.2 Hz, 1H), 2.94 (t, J=7.2 Hz, 2H), 3.81 (s, 3H), 6.17 (s, 1H), 6.85 (d, J=7.4 Hz, 2H), 6.93 (s, 1H), 7.05 (d, J=7.4 Hz, 2H), 7.15 (d, J=6.6 Hz, 2H), 7.46 (d, J=6.6 Hz, 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 25.5, 31.2, 31.6, 31.8, 32.6, 53.3, 55.2, 57.5, 63.4, 113.8, 120.1, 123.1, 125.8, 128.1, 128.7, 128.9, 133.4, 138.0, 142.6, 144.3, 145.8, 146.6, 148.2, 159.1. Anal. Calcd for $C_{33}H_{40}N_2O_3S$: C, 72.76; H, 7.40; N, 5.14. Found: C, 72.65; H, 7.55; N, 5.18.

4.7.14. *N*-[3-(4-Methoxyphenyl)-2-tosyl-cyclohexano-[*f*]isoindolinylidene]-*tert*-octylamine (8n). Isolated in 68% yield as a white solid: mp 155–158 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 1.43 (s, 6H), 1.70 (d, J=14.6 Hz, 1H), 1.73–1.78 (m, 4H), 1.98 (d, J=14.6 Hz, 1H), 2.64–2.75 (m, 2H), 2.81–2.83 (m, 2H), 3.81 (s, 3H), 6.16 (s, 1H), 6.80 (s, 1H), 6.86 (d, J=8.7 Hz, 2H), 7.10 (d, J=8.2 Hz, 2H), 7.16 (d, J=8.7 Hz, 2H), 7.47 (d, J=8.2 Hz, 2H), 7.69 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 22.6, 22.8, 29.5, 29.7, 31.1, 31.6, 31.8, 53.0, 55.2, 57.6, 63.5, 113.8, 124.5, 125.0, 128.1, 128.7, 128.9, 133.4, 136.8, 138.0, 141.0, 142.6, 144.3, 146.7, 159.1. Anal. Calcd for $C_{34}H_{42}N_2O_3S$: C, 73.08; H, 7.58; N, 5.01. Found: C, 73.07; H, 7.54; N, 4.92.

4.7.15. *N*-[3-(4-Methoxyphenyl)-2-tosyl-benzo[*f*]isoindolinylidene]-*tert*-octylamine (8o). Isolated in 31% yield as a yellow solid: mp 171–174 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9H), 1.52 (s, 3H), 1.55 (s, 3H), 1.83 (d, J=14.4 Hz, 1H), 2.13 (d, J=14.4 Hz, 1H), 2.36 (s, 3H), 3.82 (s, 3H), 6.41 (s, 1H), 6.85 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.1 Hz, 2H), 7.18 (d, J=8.8 Hz, 2H), 7.46–7.53 (m, 4H), 7.57 (s, 1H), 7.73–7.76 (m, 1H), 7.93–7.97 (m, 1H), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 31.2, 31.6, 31.9, 53.1, 55.3, 58.1, 63.5, 113.9, 123.2, 125.7, 126.4, 127.5, 127.9, 128.3, 128.6, 128.8, 129.1, 129.5, 132.5, 133.8, 134.2, 137.9, 142.8, 142.9, 146.0, 159.3. Anal. Calcd for $C_{34}H_{38}N_2O_3S$: C, 73.61; H, 6.90; N, 5.05. Found: C, 73.51; H, 6.90; N, 5.02.

4.7.16. *N*-[3-(4-Methoxyphenyl)-4,7-dimethyl-2-tosylisoindolinylidene]-*tert*-octylamine (8p). Isolated in 71% yield as a colorless crystal: mp 148–151 °C; ^{1}H NMR ($CDCl_3$) δ 0.68 (s, 9H), 1.43–1.49 (m, 7H), 1.79 (s, 3H), 1.92 (d, J=14.2 Hz, 1H), 2.22 (s, 3H), 2.51 (s, 3H), 3.75 (s, 3H), 5.66 (s, 1H), 6.75–6.77 (m, 3H), 6.85 (d, J=7.5 Hz, 1H), 6.96 (d, J=8.1 Hz, 2H), 6.99 (d, J=8.7 Hz, 2H), 7.45 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.3, 18.2, 21.3, 27.0, 31.4, 31.8, 32.0, 55.2, 59.3, 62.3, 65.0, 113.7, 127.5, 128.6, 129.4, 129.6, 129.7, 130.1, 130.4, 133.2, 133.5, 134.4, 139.7, 143.3, 143.4, 159.2. Anal. Calcd for $C_{32}H_{40}N_2O_3S$: C, 72.14; H, 7.57; N, 5.26. Found: C, 71.95; H, 7.55; N, 5.12.

4.7.17. *N*-[4,7-Dimethoxy-3-(4-methoxyphenyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8q). Isolated in 43% yield as a colorless solid: mp 145–148 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (s, 9H), 1.40 (s, 3H), 1.48 (s, 3H), 1.53 (d, J=14.3 Hz, 1H), 1.95 (d, J=14.3 Hz, 1H), 2.27 (s, 3H), 3.52 (s, 3H), 3.76 (s, 3H), 3.82 (s, 3H), 5.80 (s, 1H), 6.61 (d, J=8.6 Hz, 1H), 6.69 (d, J=8.6 Hz, 1H), 6.77 (d, J=8.6 Hz, 2H), 7.00 (d, J=8.1 Hz, 2H), 7.08 (d, J=8.6 Hz, 2H), 7.50 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3, 29.7, 31.3, 31.4, 31.8, 55.1, 55.9, 56.3, 57.1, 61.7, 62.8,

113.3, 113.5, 125.3, 128.0, 128.2, 128.5, 129.1, 130.3, 132.7, 134.6, 140.4, 143.0, 148.5, 149.9, 159.1. Anal. Calcd for $C_{32}H_{40}N_2O_5S$: C, 68.06; H, 7.14; N, 4.96. Found: C, 68.05; H, 7.19; N, 4.80.

4.7.18. A mixture of *N*-[3-(4-methoxyphenyl)-6-methyl-2-tosylisoindolinylidene]-*tert*-octylamine (8r) and *N*-[3-(4-methoxyphenyl)-5-methyl-2-tosylisoindolinylidene]-*tert*-octylamine (8′r). Isolated in 76% yield as a white solid: mp 124–128 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9H), 0.86 (s, 9H), 1.44 (s, 6H), 1.46 (s, 6H), 1.69 (d, J=14.6 Hz, 1H), 1.74 (d, J=14.6 Hz, 1H), 2.00 (d, J=15.1 Hz, 2H), 2.31 (s, 3H), 2.35 (s, 6H), 2.41 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 6.20 (s, 2H), 6.83–6.88 (m, 4H), 6.92 (s, 1H), 7.01 (d, J=7.6 Hz, 1H), 7.08–7.22 (m, 10H), 7.46 (d, J=8.1 Hz, 4H), 7.80 (s, 1H), 7.88 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 21.4, 21.6, 31.2, 31.51, 31.54, 31.72, 31.77, 31.79, 31.81, 53.15, 53.18, 55.2, 57.5, 57.7, 63.4, 63.5, 113.8, 124.2, 124.8, 124.9, 127.4, 127.6, 127.8, 128.11, 128.15, 128.71, 128.74, 128.9, 129.0, 131.9, 132.9, 133.0, 137.3, 137.79, 137.83, 141.5, 142.68, 142.70, 144.3, 146.4, 146.5, 147.2, 159.1, 159.2. Anal. Calcd for $C_{31}H_{38}N_2O_3S$: C, 71.78; H, 7.38; N, 5.40. Found: C, 71.89; H, 7.51; N, 5.22.

4.7.19. *N*-[4-Methoxy-3-(4-methoxyphenyl)-2-tosylisoindolinylidene]-*tert*-octylamine (8s). Isolated in 57% yield as a colorless crystal: mp 160–164 °C; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9H), 1.43 (s, 3H), 1.44 (s, 3H), 1.74 (d, J=14.6 Hz, 1H), 1.99 (d, J=14.6 Hz, 1H), 2.33 (s, 3H), 3.66 (s, 3H), 3.80 (s, 3H), 6.24 (s, 1H), 6.78 (d, J=8.6 Hz, 2H), 6.86 (d, J=8.1 Hz, 1H), 7.04 (d, J=8.4 Hz, 2H), 7.11 (d, J=8.6 Hz, 2H), 7.32–7.38 (m, 3H), 7.59 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 31.6, 31.8, 53.5, 55.2, 55.6, 57.8, 61.5, 112.7, 113.3, 119.6, 128.1, 128.8, 129.2, 129.3, 129.5, 131.8, 135.1, 137.8, 142.6, 146.1, 154.9, 158.9. Anal. Calcd for $C_{31}H_{38}N_2O_4S$: C, 69.63; H, 7.16; N, 5.24. Found: C, 69.67; H, 7.12; N, 5.18.

4.7.20. *N*-[3-(4-Methoxyphenyl)-7-methyl-2-tosylisoindolinylidene]-*tert*-octylamine (8t). Isolated in 56% yield as a colorless needle: mp 132–135 °C; ^{1}H NMR ($CDCl_3$) δ 0.70 (s, 9H), 1.47 (d, J=14.2 Hz, 1H), 1.50 (s, 6H), 1.94 (d, J=14.2 Hz, 1H), 2.23 (s, 3H), 2.55 (s, 3H), 3.76 (s, 3H), 5.71 (s, 1H), 6.70 (d, J=7.3 Hz, 1H), 6.77 (d, J=8.4 Hz, 2H), 6.93–7.00 (m, 4H), 7.05 (d, J=8.6 Hz, 2H), 7.48 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.6, 21.3, 27.1, 31.5, 31.8, 55.2, 59.3, 62.5, 65.9, 113.7, 121.0, 127.7, 128.8, 129.1, 129.3, 130.0, 131.0, 133.8, 134.6, 136.0, 140.9, 142.7, 143.9, 159.3. HRMS Calcd for $C_{31}H_{39}O_3N_2S$: M^++H, 519.2681. Found: m/z 519.2680.

4.7.21. *N*-[3-(4-Methoxyphenyl)-4-methyl-2-tosylisoindolinylidene]-*tert*-octylamine (8′t). Isolated in 18% yield as a colorless needle: mp 162–164 °C; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 9H), 1.42 (s, 3H), 1.45 (s, 3H), 1.74 (d, J=14.6 Hz, 1H), 1.985 (s, 3H), 1.992 (d, J=14.6 Hz, 1H), 2.32 (s, 3H), 3.81 (s, 3H), 6.20 (s, 1H), 6.81 (d, J=8.9 Hz, 2H), 7.00–7.09 (m, 4H), 7.18 (d, J=7.3 Hz, 1H), 7.24–7.35 (m, 3H), 7.87 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.3, 21.4, 31.6, 31.7, 31.9, 53.5, 55.3, 57.8, 62.8, 113.7, 125.2, 127.9, 128.1, 128.3, 128.6, 130.2, 131.1, 132.3, 134.1, 137.9, 142.6, 144.9, 146.3, 159.2. HRMS Calcd for $C_{31}H_{39}O_3N_2S$: M^++H, 519.2681. Found: m/z 519.2673.

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