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Synthesis of Fluorenes via Tandem Copper-Catalyzed [3 + 2] Cycloaddition and Rhodium-Catalyzed Denitrogenative Cyclization in a 5-*Exo* Mode from 2-Ethynylbiaryls and *N*-Sulfonyl Azides in One Pot

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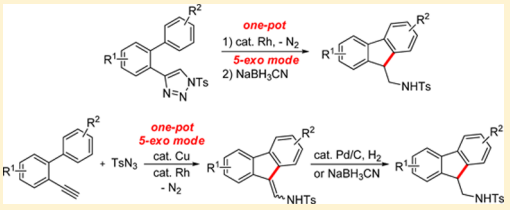
Supporting Information

ABSTRACT: An efficient synthetic method of fluorenes having an enamine moiety at C-9 methylene bridge is developed from *N*-sulfonyl-4-biaryl-1,2,3-triazole derivatives via Rh-catalyzed denitrogenative cyclization in a 5-*exo* mode. Rh-catalyzed denitrogenative cyclization followed by catalytic hydrogenation produces *N*-tosylaminomethyl-substituted fluorenes in one pot. Moreover, fluorenes are synthesized via tandem Cu-catalyzed [3 + 2] cycloaddition and Rh-catalyzed denitrogenative cyclization in a 5-*exo* mode starting from 2-ethynylbiaryls and *N*-sulfonyl azides in one pot.

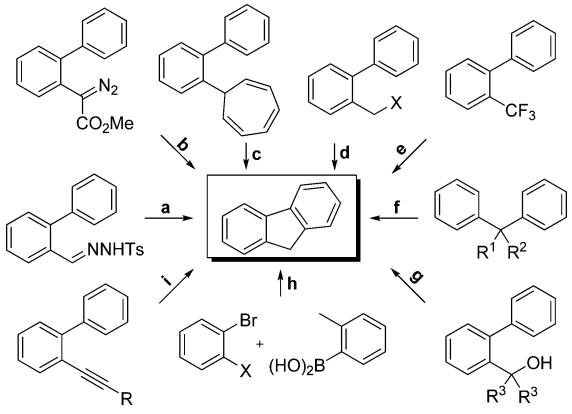


INTRODUCTION

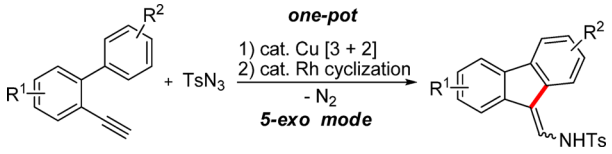
Fluorene and its derivatives have attracted a great deal of attention because of their optical and electronic properties and their function as π-conjugated materials.[1] They have been widely used as significant privileged structures in a myriad of areas such as optical agents, dyes, organic transistors, and light-emitting devices.[2] Although this functionality of fluorene derivatives has been reported, a restricted number of synthetic approaches have been demonstrated.[3] To date, intramolecular aromatic carbenoid insertion of biphenyl-2-carbaldehyde tosylhydrazones (a)[4] and biaryldiazoacetates (b),[5] retro-Büchner reaction via Au(I) carbenes (c),[6] Pd-catalyzed C−H activation using 2-phenylbenzyl halides (d),[3h] Ni-mediated double activation of C−F/C−H bonds (e),[3d] Rh-catalyzed dehydrogenative cyclization (f),[7] cyclization of *tert*-alcohols (g),[8] tandem Pd-catalyzed Suzuki cross-coupling and cyclization (h),[9] and 5-*exo*-*dig* hydroarylation of *o*-alkynyl biaryls (i)[10] were reported (Scheme 1).[11] Hence, an efficient synthesis of fluorene and its derivatives from easily available compounds has been constantly required. In particular, it is very important to prepare selectively unsymmetrically substituted fluorene derivatives and to introduce substituents at the C-9 methylene bridge of the fluorene moiety.

Recently, synthetic application of *N*-sulfonyl-1,2,3-triazoles as precursor of α-imino Rh carbenoid has been extensively reported.[12] In this regard, we developed a synthetic method of azaheterocyclic compounds including pyrroles, dihydroazepines, dihydropyrroles, and bicyclic *N*,*O*-acetals and Rh-catalyzed diastereoselective *N*-sulfonylaminoalkenylation of azulenes using *N*-sulfonyltriazoles.[13] These results encouraged us to investigate the feasibility of synthesis of fluorenes using *N*-sulfonyl-4-biaryl-1,2,3-triazole derivatives. Herein, we report a synthetic approach of fluorenes having an enamine moiety at the C-9 methylene bridge from *N*-sulfonyl-4-biaryl-1,2,3-triazole derivatives via Rh-catalyzed denitrogenative cyclization in a 5-*exo* mode (Scheme 2). In addition, synthesis of fluorene

Scheme 1. Previously Reported Synthetic Methods of Fluorenes



Scheme 2. Synthesis of Fluorenes via Tandem Cu-Catalyzed [3 + 2] Cycloaddition and Rh-Catalyzed Denitrogenative Cyclization



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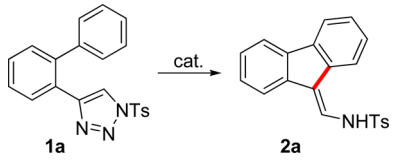
derivatives via Cu-catalyzed [3 + 2] cycloaddition followed by Rh-catalyzed denitrogenative cyclization is demonstrated starting from 2-ethynylbiaryls and *N*-sulfonylazides in one pot.

RESULTS AND DISCUSSION

We started our investigations with *N*-tosyl-4-(2-biphenyl)-1,2,3-triazole (**1a**) obtained from [3 + 2] cycloaddition of 2-ethynylbiphenyl with tosyl azide in the presence of CuTC (Table 1).[14] However, $Cu(OAc)_2$, $Cu(OTf)_2$, and $Cu(acac)_2$

Table 1. Reaction Optimization[a]



1a 2a

entry	cat. (mol %)	solvent	time (h)	temp (°C)	yield[b] (%)
1	$Cu(OAc)_2$ (5.0)	$CHCl_3$	60	12	0
2	$Cu(OTf)_2$ (5.0)	$CHCl_3$	60	12	0
3	$Cu(acac)_2$ (5.0)	$CHCl_3$	60	12	0
4	$Rh_2(tfa)_4$ (1.0)	$CHCl_3$	60	12	0
5	$Rh_2(pfb)_4$ (1.0)	$CHCl_3$	60	12	0
6	$Rh_2(OAc)_4$ (1.0)	$CHCl_3$	60	12	20
7	$Rh_2(oct)_4$ (1.0)	$CHCl_3$	60	12	44
8	$Rh_2(esp)_2$ (1.0)	$CHCl_3$	60	12	50
9	$Rh_2(esp)_2$ (1.0)	DCE	80	12	48
10	$Rh_2(esp)_2$ (1.0)	ethyl acetate	80	12	0
11	$Rh_2(esp)_2$ (1.0)	dioxane	80	12	0
12	$Rh_2(esp)_2$ (1.0)	toluene	80	1	99 (99)[c]

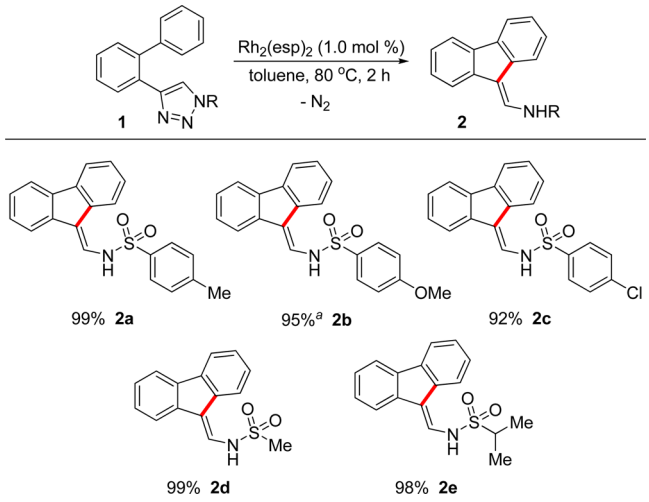
[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv) and catalyst (1−5 mol %) were used in solvent (3.0 mL) under N_2 atmosphere. [b]NMR yield with CH_2Br_2 as an internal standard. [c]Isolated yield.

and electron-deficient dirhodium complexes such as $Rh_2(tfa)_4$ and $Rh_2(pfb)_4$ as catalyst are totally ineffective (entries 1−5). Gratifyingly, $Rh_2(OAc)_4$ in $CHCl_3$ gave fluorene **2a** in 20% yield (entry 6). Among the catalysts examined, $Rh_2(esp)_2$ afforded **2a** in 50% yield (entry 8). Next, a myriad of solvents such as $CHCl_3$, DCE, ethyl acetate, dioxane, and toluene were screened. To our delight, reaction in toluene provided the desired product **2a** in quantitative yield via intramolecular denitrogenative cyclization in a 5-*exo* mode (entry 12). The structure of **2a** was unambiguously determined by X-ray crystallography (see the Supporting Information).

First, a wide range of *N*-sulfonyl groups on the biphenyl-1,2,3-triazole ring **1** were screened in the Rh-catalyzed denitrogenative cyclization (Scheme 3). (Benzenesulfonyl)-triazoles bearing electron-donating methyl and methoxy groups and an electron-withdrawing chloro group afforded the denitrogenative cyclization products **2a**, **2b**, and **2c** in excellent yields ranging from 92% and 99% in a 5-*exo* mode. Moreover, methane- and isopropanesulfonyl triazoles produced fluorenes **2d** and **2e** in 99% and 98% yields, respectively, indicating that a modification of the sulfonyl groups at the N1 of triazole **1** did not effect on the efficiency of denitrogenative cyclization.

Having the optimized conditions, we then studied the scope of the current procedure by examining a variety of substituents on arene moiety of the *N*-tosyl-4-biaryl-1,2,3-triazole derivatives **1** (Scheme 4). Electronic modification of substituents on the phenyl ring of **1** did not largely influence efficiency of the reaction. For example, *N*-tosyl-4-(2-biaryl)-1,2,3-triazoles pos-

Scheme 3. Effects of Sulfonyl Groups on Rh-Catalyzed Denitrogenative Cyclization*



1 2

99% **2a** 95%[a] **2b** 92% **2c**

99% **2d** 98% **2e**

*Reaction conditions: **1** (0.3 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (1.0 mol %) were used in toluene (3.0 mL). [a]$Rh_2(esp)_2$ (2.0 mol %) was used.

sessing electron-donating 2-methyl, 4-*tert*-butyl, and 4-methoxy groups on the phenyl ring underwent the Rh-catalyzed denitrogenative cyclization in a 5-*exo* mode, producing the desired unsymmetrical fluorenes (**2j**, **2f**, and **2g**) in good to excellent yields ranging from 85% and 99%. In addition, electron-withdrawing 4-chloro and 4-trifluoromethyl groups on the phenyl ring afforded the denitrogenative cyclization products (**2h** and **2i**) in excellent yields. When triazoles (**1k** and **1l**) having 3-methyl and 3-chloro groups on the phenyl ring were treated with Rh catalyst, fluorenes **2k** and **2l** were obtained in 97% (1.2:1) and 97% (1.2:1) yields, respectively. When sterically constrained Rh catalysts such as $Rh_2(S\text{-DOSP})_4$ and $Rh_2(S\text{-PTAD})_4$ were employed for the cyclization, the regioselectivity was increased. However, the cyclization was not completed, and then the triazoles were recovered (Table 2). *N*-Tosyl-4-biaryl-1,2,3-triazoles **1** bearing 2,4-difluoro, 3,5-dimethyl, and 3,5-dichloro groups were smoothly cyclized as well in a 5-*exo* mode. The stereochemistry of **2n** was determined by NOE and HSQC (see the Supporting Information). It was noteworthy that triazoles having 2-furyl and 2-thiophenyl groups were also successfully applied to the current Rh-catalyzed denitrogenative cyclization conditions, producing **2p** (72%) and **2q** (96%). We observed that variation of substituents such as methyl and fluoro group on the arene moiety directly attached to triazole ring did not affect the reaction efficiency. Under the optimized conditions, the desired fluorenes **2r** and **2s** were obtained in 95% and 99% yields, respectively. Fluorene **2t** was selectively produced in 99% yield from triazole **1t** possessing 1-naphthyl group without the formation of 3,4-fused dihydroindole via intramolecular dearomatizing [3 + 2] annulation in a 6-*exo* mode (eq 1).[12n]

The synthetic utility of the Rh-catalyzed denitrogenative cyclization was demonstrated by its successful preparation of fluorenes **2** directly from 2-ethynylbiaryl derivatives **3** in one pot (Scheme 5). For instance, 2-ethynylbiphenyl (**3a**), TsN_3 (1.0 equiv), CuTC (10 mol %), $Rh_2(esp)_2$ (1.0 mol %), and toluene were placed all together in a reaction flask. Then, the reaction mixture was stirred at room temperature for 2 h, during which **3a** was completely transformed to the biphenyl *N*-triazole **1a**. After it was further stirred at 80 °C for 1 h, the

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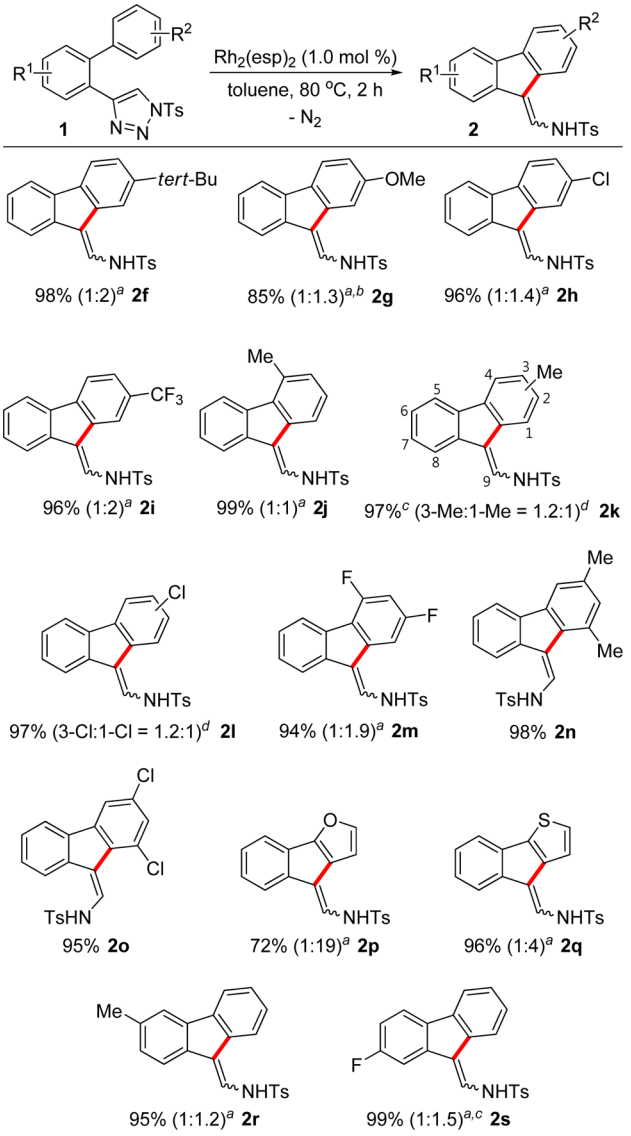
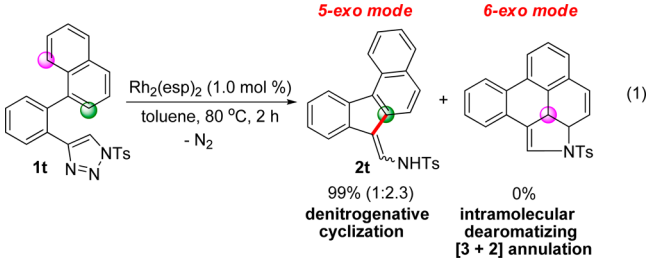
Scheme 4. Synthesis of Fluorenes via Rh-Catalyzed Denitrogenative Cyclization*

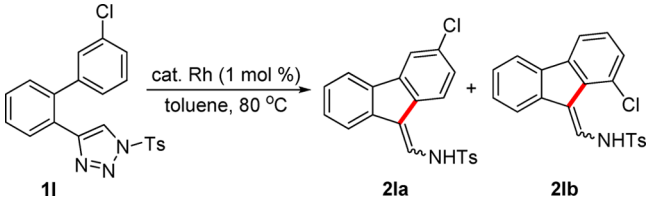


*Reaction conditions: **1** (0.3 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (1.0 mol %) were used in toluene (3.0 mL). [a]Numbers in parentheses are isomeric ratio of double bond in enamine. [b]Six h. [c]$Rh_2(esp)_2$ (2.0 mol %) was used. [d]Numbers in parentheses are ratio of constitutional isomers arising from position of methyl and chloro group on the aryl ring.



desired fluorene **2a** was produced in 60% yield in a 5-*exo* mode. The presence of *tert*-butyl, trifluoromethyl, methyl, and fluoro groups on the phenyl ring of 2-ethynylbiaryl derivatives did not significantly affect the reaction efficiency, thus enabling the preparation of fluorenes directly from the alkynes **3** in a 5-*exo* mode in one pot. These results indicate that the copper catalyst remaining in the reaction mixture after the [3 + 2] cycloaddition reaction does not affect the formation and reactivity of the Rh carbenoid.

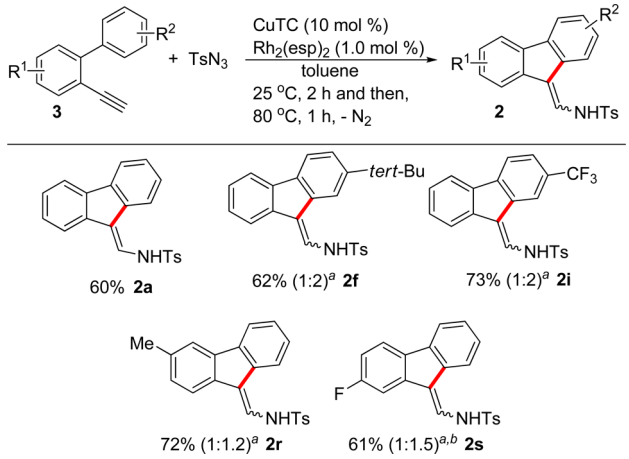
Table 2. Effects of Sterically Constrained Rh Catalysts on Denitrogenative Cyclization[a]



entry	cat. Rh	time (h)	yield (%) 2l (2la:2lb)	yield (%) 1l
1	$Rh_2(esp)_2$	3	97 (1.2:1)	0
2	Rh_2(*S*-DOSP)$_4$	5	63 (4.5:1)	36
3	Rh_2(*S*-PTAD)$_4$	5	60 (15:1)	27

[a]Reaction conditions: **1l** (0.3 mmol, 1.0 equiv) and Rh catalyst (1.0 mol %) were used in toluene (3.0 mL).

Scheme 5. Synthesis of Fluorenes via Tandem Cu-Catalyzed [3 + 2] Cycloaddition and Rh-Catalyzed Denitrogenative Cyclization in One Pot*



*Reaction conditions: **3** (0.3 mmol, 1.0 equiv), TsN_3 (0.3 mmol), CuTC (0.03 mmol), and $Rh_2(esp)_2$ (1.0 mol %) were used in toluene (3.0 mL) at 25 °C for 1 h and then at 80 °C for 1 h. NMR yield of **2** with CH_2Br_2 as an internal standard. [a]Numbers in parentheses are isomeric ratio of double bond in enamine. [b]$Rh_2(esp)_2$ (2.0 mol %) was used.

When the fluorenes **2** having an enamine moiety at the C-9 methylene bridge were treated with hydrogen gas in the presence of Pd/C, hydrogenation reaction smoothly took place to provide *N*-tosylaminomethyl-substituted fluorenes **4** (Scheme 6). Reduction of **2a** with H_2 and Pd/C afforded the desired product **4a** in quantitative yield. Fluorenes **2** having a variety of substituents including methyl, dimethyl, *tert*-butyl, methoxy, chloro, fluoro, difluoro, and trifluoromethyl on the arene moiety were subjected to the reduction, resulting in the formation of **4b**−**m** in excellent yields ranging from 92% to 99%. The present hydrogenation worked equally well with fluorenes (**4j** and **4k**) possessing 1-naphthyl and 2-thiophenyl moieties.

With the success of above cyclizations and reductions, we next attempted synthesis of *N*-tosylaminomethyl-substituted

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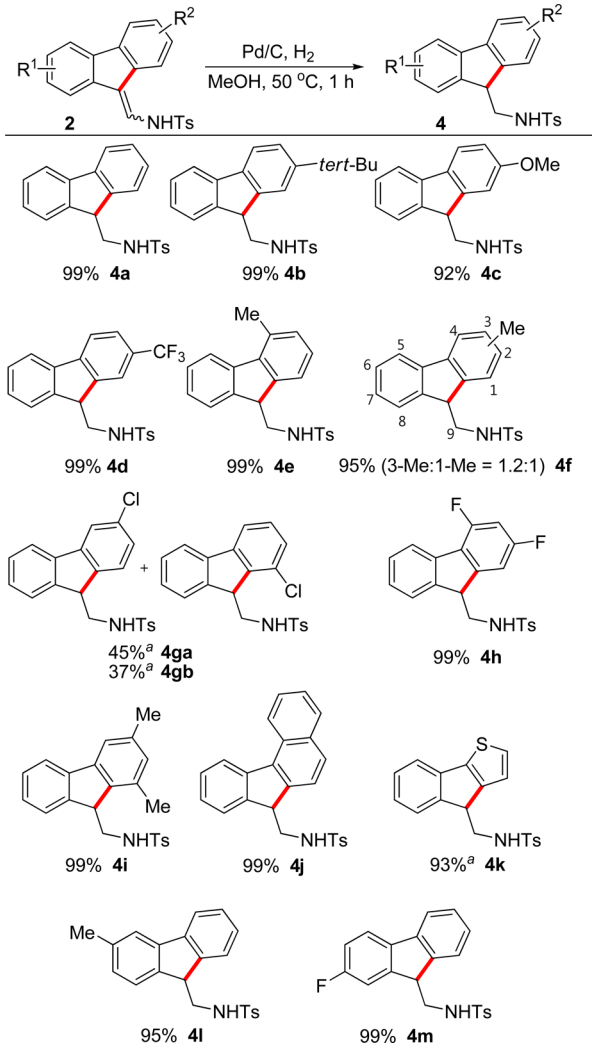
Scheme 6. Synthesis of Aminomethyl-Substituted Fluorenes via Hydrogenation*



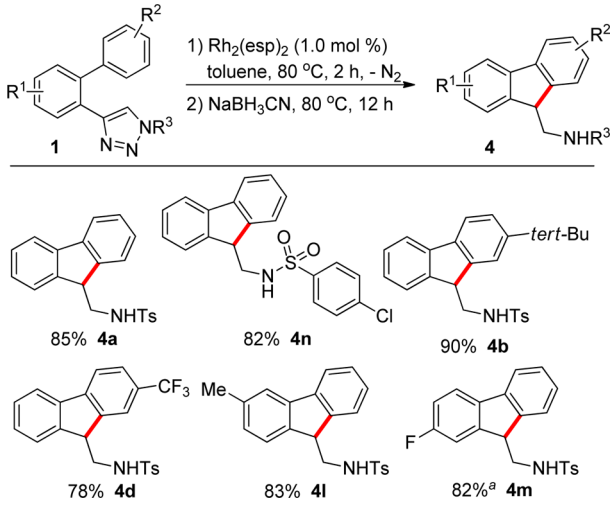
*Reaction conditions: **2** (0.15 mmol, 1.0 equiv) and Pd/C (10 wt % of **2**) were used in MeOH (1.5 mL) at 50 °C for 1 h. [a]**2** (0.15 mmol, 1.0 equiv) and $NaBH_3CN$ (2 equiv) were used in toluene (1.5 mL) at 80 °C for 12 h.

fluorenes directly from 2-biaryltriazoles via Rh-catalyzed denitrogenative cyclization followed by reduction in one pot (Scheme 7). First, 2-biphenyltriazole **1a** was treated with $Rh_2(esp)_2$ in toluene at 80 °C for 2 h, during which time **1a** was cyclized to the fluorene **2a**, and then the reaction mixture was cooled to room temperature. Next, $NaBH_3CN$ was added to the reaction mixture, which was further stirred at 80 °C for 12 h, producing **4a** in 85% yield in one pot. In the case of *N*-4-chlorobenzenesulfonyltriazole **1c**, the desired fluorene **4n** was obtained in 82% yield. Rh-catalyzed denitrogenative cyclization followed by reduction in one pot turned out to be compatible with the triazoles having *tert*-butyl, trifluoromethyl, methyl, and fluoro groups on the phenyl ring.

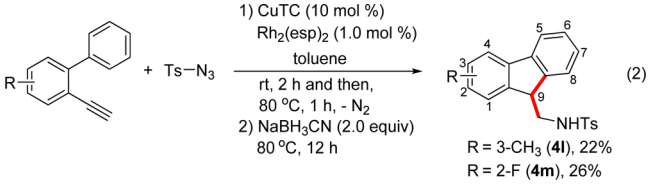
However, attempts to synthesize aminomethyl-substituted fluorenes directly from alkynes through a sequence of [3 + 2] cycloaddition−denitrogenative cyclization−reduction gave the desired products **4l** and **4m** in low yields (eq 2).

A plausible mechanism for the preparation of fluorenes **2** from *N*-sulfonyl-4-(2-biaryl)-1,2,3-triazoles **1** is shown in

Scheme 7. Synthesis of Aminomethyl-Substituted Fluorenes via Rh-Catalyzed Denitrogenative Cyclization followed by Reduction in One Pot*

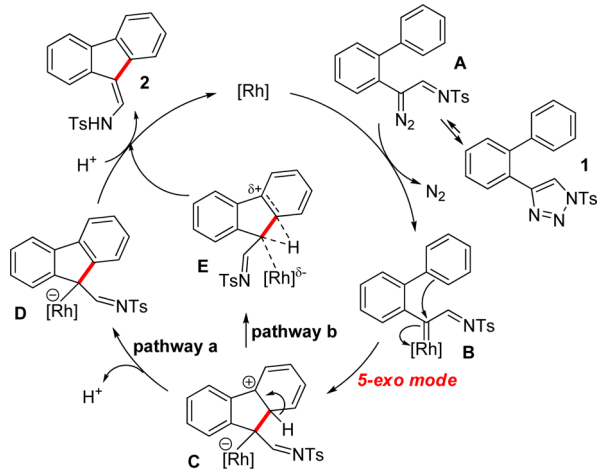


*Reaction conditions: **1** (0.3 mmol, 1.0 equiv) and $Rh_2(esp)_2$ (1.0 mol %) were used in toluene (3.0 mL) at 80 °C for 2 h and then, $NaBH_3CN$ (0.6 mmol) was added. [a]$Rh_2(esp)_2$ (2.0 mol %) was used.



Scheme 8. First, a reversible ring−chain tautomerization of **1** provides *α*-diazo imine **A**.[15] The following irreversible reaction

Scheme 8. Plausible Mechanism



of **A** with rhodium(II) catalyst affords *α*-imino rhodium(II) carbenoid **B** together with release of nitrogen gas. The carbenoid carbon of **B** is electrophilic enough to bring about the cyclization via the intramolecular attack of the phenyl ring in a 5-*exo* mode to produce the Rh-bound zwitterionic intermediate **C**. Next, rearomatization followed by proto-derhodation might produce the desired fluorenes **2** (pathway a). In addition, it has proposed that the following 1,2-hydrogen shift from an aryl carbon to the carbon center occurs upon the

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rearomatization of the ring system to provide the desired fluorene **2** (pathway b).[5] The present reaction is in marked contrast to the synthesis of tricyclic 3,4-fused dihydroindoles via the Rh-catalyzed dearomatizing [3 + 2] annulation reaction of 4-(3-arylpropyl)-1,2,3-triazoles in a 6-*exo* mode.[12n]

CONCLUSION

In summary, we have developed an efficient synthetic method of fluorenes having enamine moiety at C-9 methylene bridge from *N*-sulfonyl-4-biaryl-1,2,3-triazole derivatives via Rh-catalyzed denitrogenative cyclization in a 5-*exo* mode. Rh-catalyzed denitrogenative cyclization followed by catalytic hydrogenation produces the aminomethyl-substituted fluorenes in one pot. Moreover, this protocol can be applied to the synthesis of fluorenes via tandem Cu-catalyzed [3 + 2] cycloaddition and Rh-catalyzed denitrogenative cyclization starting from 2-ethynylbiaryls and *N*-sulfonylazides in one pot.

EXPERIMENTAL SECTION

General Methods. Reactions were carried out in oven-dried glassware under air atmosphere. $Cu(acac)_2$, $Cu(OTf)_2$, $Cu(OAc)_2$, $Rh_2(oct)_4$, $Rh_2(OAc)_4$, $Rh_2(pfb)_4$, $Rh_2(tfa)_4$, $Rh_2(esp)_2$, Rh_2(*S*-DOSP)$_4$, and Rh_2(*S*-PTAD)$_4$ were purchased and used as received. Commercial available reagents were used without purification. DCE, $CHCl_3$, EtOAc, 1,4-dioxane, and toluene were dried with CaH_2. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light and then developed using a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230−400 mesh). ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on an NMR spectrometer. Deuterated chloroform, acetone, and benzene were used as the solvents, and chemical shift values (δ) are reported in parts per million relative to the residual signals of these solvent [δ 7.26 for ^{1}H (chloroform-*d*), δ 7.16 for ^{1}H (benzene-d_6), δ 2.05 for ^{1}H (acetone-d_6), δ 77.2 for ^{13}C{^{1}H} (chloroform-*d*), δ 128.1 for ^{13}C{^{1}H} (benzene-d_6) and δ 29.8, 206.2 for ^{13}C{^{1}H} (acetone-d_6)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Mass spectrometry was performed on GC/HRMS spectrometer under electron impact (EI) ionization technique (magnetic sector−electric sector double-focusing mass analyzer). Melting points were determined in an open capillary tube.

Starting Materials of 4-(Biaryl-2-yl)-1-sulfonyl-1*H*-1,2,3-triazoles (1) and 2-Ethynyl-1,1′-biaryls (3).[14b,16] *4-([1,1′-Biphenyl]-2-yl)-1-tosyl-1H-1,2,3-triazole* (***1a***): white solid; mp 87−91 °C; R_f = 0.2 (EtOAc/hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.05 (m, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.47−7.39 (m, 3H), 7.36−7.32 (m, 5H), 7.17−7.15 (m, 2H), 6.95 (s, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 146.3, 141.1, 140.9, 133.3, 130.5, 130.3, 129.2, 129.04, 128.97, 128.8, 128.6, 128.0, 127.8, 127.6, 121.8, 22.0; IR (neat) 3058, 3029, 1594, 1475, 1394, 1347, 1251, 1195 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{21}H_{17}N_3O_2S$ 375.1041, found 375.1039.

4-(Biphenyl-2-yl)-1-(4-methoxyphenylsulfonyl)-1H-1,2,3-triazole (***1b***): white solid; mp 107−111 °C; R_f = 0.1 (EtOAc/hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 1H), 7.87 (d, *J* = 9.1 Hz, 2H), 7.48−7.39 (m, 3H), 7.37−7.33 (m, 3H), 7.18−7.16 (m, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.95 (s, 1H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 146.2, 141.1, 140.9, 131.1, 130.3, 129.3, 129.0, 128.9, 128.8, 128.1, 127.8, 127.7, 127.2, 121.7, 115.1, 56.1; IR (neat) 3160, 3060, 1592, 1318, 1268, 1197, 1167, 1021 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{21}H_{17}N_3O_3S$ 391.0991, found 391.0994.

4-(Biphenyl-2-yl)-1-(4-chlorophenylsulfonyl)-1H-1,2,3-triazole (***1c***): white solid; mp 97−101 °C; R_f = 0.4 (EtOAc/hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.05 (m, 1H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.47−7.44 (m, 2H), 7.43−7.40 (m, 1H), 7.37−7.33 (m, 3H), 7.18−7.15 (m, 2H), 6.94 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.5, 142.8, 141.1, 140.9, 134.7, 130.4, 130.3, 130.0, 129.3, 129.14, 129.08, 128.8, 128.1, 127.9, 127.4, 121.8; IR (neat) 3095, 3062, 1584, 1476, 1345, 1194, 1166, 1086 cm^{-1}; HRMS (EI) *m*/*z* calcd $C_{20}H_{14}ClN_3O_2S$ 395.0495, found 395.0496.

4-(Biphenyl-2-yl)-1-(methylsulfonyl)-1H-1,2,3-triazole (***1d***): white solid; mp 126−130 °C; R_f = 0.3 (EtOAc/hexane = 1:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.14 (m, 1H), 7.53−7.45 (m, 2H), 7.42−7.36 (m, 4H), 7.24−7.22 (m, 2H), 6.95 (s, 1H), 3.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.3, 141.03, 141.02, 130.5, 129.19, 129.16, 129.1, 128.9, 128.15, 128.08, 127.3, 121.4, 42.7; IR (neat) 3154, 3025, 1643, 1475, 1323, 1228, 1184 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{15}H_{13}N_3O_2S$ 299.0725, found 299.0725.

4-(Biphenyl-2-yl)-1-(isopropylsulfonyl)-1H-1,2,3-triazole (***1e***): white solid; mp 81−85 °C; R_f = 0.3 (EtOAc/hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.09 (m, 1H), 7.53−7.45 (m, 2H), 7.38−7.36 (m, 4H), 7.23−7.21 (m, 2H), 6.96 (s, 1H), 3.70 (septet, *J* = 6.7 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.0, 141.1, 141.0, 130.4, 129.22, 129.18, 129.1, 128.8, 128.1, 127.9, 127.5, 123.3, 57.4, 16.0; IR (neat) 3157, 3060, 1475, 1347, 1321, 1179, 1157, 986 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{17}H_{17}N_3O_2S$ 327.1041, found 327.1040.

4-(4′-tert-Butylbiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (***1f***): white solid; mp 128−132 °C; R_f = 0.3 (EtOAc/hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11−8.09 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.47−7.41 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 3H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 2.45 (s, 3H), 1.42 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.2, 147.2, 146.2, 140.8, 138.2, 133.4, 130.4, 130.3, 128.9, 128.8, 128.6, 127.9, 127.8, 125.7, 121.8, 34.8, 31.6, 22.0; IR (neat) 3060, 3029, 1594, 1396, 1346, 1195, 1176, 986 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{25}H_{25}N_3O_2S$ 431.1667, found 431.1665.

4-(4′-Methoxybiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (***1g***): white solid; mp 98−102 °C; R_f = 0.3 (EtOAc/hexane =1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.45−7.39 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.34−7.31 (m, 1H), 7.08−7.05 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 147.3, 146.5, 140.6, 133.4, 133.3, 130.6, 130.5, 130.4, 129.2, 129.0, 128.6, 127.8, 121.9, 114.2, 55.5, 22.0; IR (neat) 3154, 3060, 1611, 1515, 1479, 1346, 1296, 1176, 1035 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{22}H_{19}N_3O_3S$ 405.1147, found 405.1143.

4-(4′-Chlorobiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (***1h***): white solid; mp 103−107 °C; R_f = 0.3 (EtOAc/hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.93 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.49−7.44 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.33−7.30 (m, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.12 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.4, 146.4, 139.7, 139.4, 133.8, 133.3, 130.7, 130.6, 130.2, 129.6, 129.3, 128.8, 128.6, 128.4, 127.7, 121.9, 22.0; IR (neat) 3069, 2982, 1614, 1467, 1366, 1182, 1088, 1033 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{21}H_{16}ClN_3O_2S$ 409.0652, found 409.0650.

1-Tosyl-4-(4′-(trifluoromethyl)biphenyl-2-yl)-1H-1,2,3-triazole (***1i***): white solid; mp 105−109 °C; R_f = 0.2 (EtOAc/hexane = 1:10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (m, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.54−7.45 (m, 4H), 7.38−7.33 (m, 3H), 7.27−7.25 (m, 2H), 7.11 (s, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.5, 146.1, 144.7, 139.5, 133.2, 130.5, 130.2, 129.82, 129.79, 129.77 (q, *J* = 32.4 Hz), 129.3, 128.7, 128.5, 127.6, 125.5 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.2 Hz), 121.8, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.4; IR (neat) 3149, 3065, 1617, 1594, 1402, 1325, 1196, 1107, 987 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{22}H_{16}F_3N_3O_2S$ 443.0915, found 443.0912.

4-(2′-Methylbiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (***1j***): white solid; mp 124−128 °C; R_f = 0.5 (EtOAc/hexane = 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.22 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.49−7.38 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30−7.23 (m, 3H), 7.12−7.10 (m, 1H), 6.66 (s, 1H), 2.45 (s, 3H), 1.81 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 146.0, 140.8, 139.9, 135.9, 133.3, 130.5, 130.4, 130.0, 129.4, 129.0, 128.5, 128.4, 128.3, 128.0, 127.8, 126.6, 120.9, 22.0, 19.7; IR (neat) 3154, 3054, 1593, 1394, 1345, 1195, 1176, 1093 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{22}H_{19}N_3O_2S$ 389.1198, found 389.1200.

4-(3′-Methylbiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (***1k***): white solid; mp 85−89 °C; R_f = 0.3 (EtOAc/hexane =1:10); ^{1}H NMR

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(400 MHz, $CDCl_3$) δ 8.09−8.06 (m, 1H), 7.82 (d, J = 8.5 Hz, 2H), 7.46−7.39 (m, 2H), 7.36−7.34 (m, 2H), 7.33−7.31 (m, 1H), 7.24−7.22 (m, 2H), 7.00 (s, 1H), 6.98 (s, 1H), 6.96−6.94 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 146.3, 141.1, 141.0, 138.5, 133.3, 130.5, 130.3, 129.9, 128.94, 128.91, 128.62, 128.60, 128.5, 128.0, 127.6, 126.3, 121.8, 22.0, 21.5; IR (neat) 3154, 3054, 1593, 1393, 1347, 1195, 1176, 764 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}N_3O_2S$: 389.1198, found 389.1199.

4-(3′-Chloro-[1,1′-biphenyl]-2-yl)-1-tosyl-1H-1,2,3-triazole (**1l**): white solid; mp 123−127 °C; R_f = 0.3 (EtOAc/hexane = 1:5); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.01 (m, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.50−7.36 (m, 5H), 7.26−7.31 (m, 2H), 7.15 (t, J = 1.7 Hz, 1H), 7.08 (dt, J = 7.5, 1.3 Hz, 1H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.4, 145.9, 142.9, 139.3, 134.5, 133.2, 130.6, 130.3, 130.1, 129.4, 129.3, 129.2, 128.6, 128.5, 127.9, 127.6, 127.5, 121.7, 22.0; IR (neat) 3152, 3060, 1593, 1393, 1348, 1195, 1176, 1094, 764 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{16}ClN_3O_2S$ 409.0652, found 409.0648.

4-(2′,4′-Difluorobiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (**1m**): white solid; mp 109−113 °C; R_f = 0.3 (EtOAc/hexane = 1:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.52−7.44 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.33−7.31 (m, 1H), 7.28 (s, 1H), 7.17−7.11 (m, 1H), 6.90−6.85 (m, 1H), 6.78−6.73 (m, 1H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8 (dd, J = 250.0, 11.3 Hz), 159.5 (dd, J = 249.6, 11.8 Hz), 147.4, 146.2, 133.5, 133.2, 132.4 (dd, J = 9.4, 4.6 Hz), 131.1, 130.5, 129.3, 129.2, 128.9, 128.7, 128.6, 124.6 (dd, J = 16.4, 4.0 Hz), 120.8, 111.8 (dd, J = 21.1, 3.8 Hz), 104.4 (t, J = 25.6 Hz), 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −109.6 (quintet, J = 7.8 Hz, 1F), −110.3 (q, J = 8.6 Hz, 1F); IR (neat) 3148, 3066, 1619, 1321, 1267, 1196, 1140, 1103, 766 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{15}F_2N_3O_2S$ 411.0853, found 411.0850.

4-(3′,5′-Dimethylbiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (**1n**): white solid; mp 106−110 °C; R_f = 0.3 (EtOAc/hexane = 1:10); ^1H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.45−7.38 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.32−7.29 (m, 1H), 7.04 (s, 1H), 7.00 (s, 1H), 6.79 (s, 2H), 2.45 (s, 3H), 2.28 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 146.3, 141.1, 141.0, 138.3, 133.4, 130.5, 130.3, 129.4, 128.8, 128.5, 127.8, 127.5, 126.9, 121.7, 21.9, 21.4; IR (neat) 3156, 3023, 1595, 1395, 1321, 1176, 765 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{21}N_3O_2S$ 403.1354, found 403.1357.

4-(3′,5′-Dichlorobiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (**1o**): white solid; mp 134−138 °C; R_f = 0.3 (EtOAc/hexane = 1:10); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99−7.97 (m, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.51−7.43 (m, 2H), 7.40−7.37 (m, 3H), 7.31−7.28 (m, 2H), 7.07 (d, J = 1.8 Hz, 2H), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.5, 145.7, 144.0, 138.0, 135.2, 133.1, 130.7, 130.3, 129.8, 129.4, 129.0, 128.6, 127.9, 127.8, 127.4, 121.6, 22.0; IR (neat) 3142, 3069, 1393, 1348, 1195, 1176, 1097, 688 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{15}Cl_2N_3O_2S$ 443.0206, found 443.0206.

4-(2-(Furan-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (**1p**): white solid; mp 117−121 °C; R_f = 0.3 (EtOAc/hexane = 1:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.88−7.86 (m, 1H), 7.57−7.55 (m, 1H), 7.47−7.37 (m, 6H), 6.44 (dd, J = 2.8, 1.7 Hz, 1H), 6.22 (d, J = 3.0 Hz, 1H), 2.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.8, 147.4, 146.2, 142.2, 133.3, 130.6, 129.9, 129.8, 129.7, 129.2, 128.8, 127.6, 121.6, 111.8, 109.0, 22.0; IR (neat) 3148, 3066, 2847, 1589, 1442, 1394, 1195, 1174, 1035 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}N_3O_3S$ 365.0834, found 365.0833.

4-(2-(Thiophene-2-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (**1q**): white solid; mp 89−93 °C; R_f = 0.3 (EtOAc/hexane = 1:8); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03−8.00 (m, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.47−7.35 (m, 6H), 7.26 (s, 1H), 7.04 (dd, J = 5.1, 3.5 Hz, 1H), 6.83 (dd, J = 3.5, 1.1 Hz, 1H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.3, 145.8, 141.8, 133.3, 133.2, 131.5, 130.5, 129.3, 128.9, 128.89, 128.86, 128.6, 127.5, 127.1, 126.4, 121.7, 21.9; IR (neat) 3146, 3058, 1593, 1346, 1194, 1174, 985 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}N_3O_2S_2$ 381.0606, found 381.0609.

4-(5-Methylbiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (**1r**): white solid; mp 71−75 °C; R_f = 0.3 (EtOAc/hexane = 1:10); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.43−7.38 (m, 1H), 7.36−7.32 (m, 4H), 7.28−7.25 (m, 1H), 7.17−7.14 (m, 3H), 6.91 (s, 1H), 2.45 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 146.4, 141.3, 140.7, 139.0, 133.4, 131.1, 130.5, 129.2, 129.0, 128.8, 128.7, 128.6, 127.8, 124.8, 121.4, 22.0, 21.4; IR (neat) 3157, 3057, 1594, 1345, 1194, 1178, 985 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}N_3O_2S$ 389.1198, found 389.1196.

4-(4-Fluorobiphenyl-2-yl)-1-tosyl-1H-1,2,3-triazole (**1s**): white solid; mp 114−118 °C; R_f = 0.3 (EtOAc/hexane = 1:7); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84−7.80 (m, 3H), 7.47−7.42 (m, 1H), 7.40−7.35 (m, 4H), 7.31−7.28 (m, 1H), 7.17−7.10 (m, 3H), 6.91 (s, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 246.8 Hz), 147.4, 145.2 (d, J = 2.3 Hz), 140.2, 136.8 (d, J = 3.4 Hz), 133.1, 132.0 (d, J = 8.1 Hz), 130.5, 129.3, 128.9, 128.6, 128.1, 121.9, 115.9, 115.7 (d, J = 2.3 Hz), 115.4, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.2; IR (neat) 3157, 3066, 1611, 1594, 1482, 1322, 1257, 1177, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{16}FN_3O_2S$ 393.0947, found 393.0946.

4-(2-(Naphthalen-1-yl)phenyl)-1-tosyl-1H-1,2,3-triazole (**1t**): white solid; mp 129−133 °C; R_f = 0.4 (EtOAc/hexane = 1:5); ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, J = 7.7, 1.4 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.58−7.54 (m, 2H), 7.52−7.48 (m, 1H), 7.45−7.36 (m, 5H), 7.32−7.30 (m, 1H), 7.22−7.17 (m, 3H), 6.44 (s, 1H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.8, 145.8, 138.9, 138.6, 133.6, 133.1, 131.5, 131.2, 130.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.2, 126.6, 126.2, 125.8, 125.6, 121.2, 21.9; IR (neat) 3160, 3057, 1593, 1485, 1393, 1321, 1195, 1175 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{19}N_3O_2S$ 425.1198, found 425.1195.

2-Ethynyl-1,1′-biphenyl (**3a**)[17a]: colorless oil; R_f = 0.5 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67−7.59 (m, 3H), 7.50−7.32 (m, 6H), 3.05 (s, 1H); $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 140.3, 133.9, 129.6, 129.3, 129.0, 128.0, 127.6, 127.1, 120.7, 83.0, 80.1.

4′-tert-Butyl-2-ethynyl-1,1′-biphenyl (**3f**)[17b]: colorless oil; R_f = 0.55 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.37−7.41 (m, 5H), 7.23−7.31 (m, 1H), 3.03 (s, 1H), 1.36 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.5, 144.9, 139.7, 133.9, 129.6, 128.9, 127.8, 126.9, 126.8, 126.1, 124.3, 120.4, 83.4, 80.0, 34.9, 31.3.

2-Ethynyl-4′-(trifluoromethyl)biphenyl (**3i**): yellow oil; R_f = 0.4 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.67−7.64 (m, 1H), 7.47−7.43 (m, 1H), 7.38−7.34 (m, 2H), 3.07 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 143.0, 134.1, 129.74, 129.73 (q, J = 32.5 Hz), 129.6, 129.3, 127.9, 125.1 (q, J = 3.7 Hz), 124.4 (q, J = 272.2 Hz), 120.6, 82.7, 80.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.4; IR (neat) 3303, 3062, 3023, 1618, 1478, 1325, 1166, 1125, 763 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_9F_3$ 246.0656, found 246.0656.

2-Ethynyl-5-methyl-1,1′-biphenyl (**3r**): yellow oil; R_f = 0.2 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.57 (m, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.44−7.34 (m, 3H), 7.19 (s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 2.99 (s, 1H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 140.5, 139.3, 133.9, 130.5, 129.3, 128.1, 128.0, 127.6, 117.6, 83.4, 79.5, 21.6; IR (neat) 3288, 3021, 2102, 1603, 1485, 1072, 819 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{12}$ 192.0939, found 192.0939.

2-Ethynyl-4-fluorobiphenyl (**3s**): yellow oil; R_f = 0.3 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.45−7.36 (m, 3H), 7.36−7.29 (m, 2H), 7.11 (td, J = 12.6, 2.75 Hz, 1H), 3.06 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5 (d, J = 246.8 Hz), 140.8 (d, J = 3.5 Hz), 139.4, 131.4 (d, J = 8.6 Hz), 129.4, 128.2, 127.8, 122.2 (d, J = 9.4 Hz), 120.3 (d, J = 23.1 Hz), 116.5 (d, J = 21.2 Hz), 82.1 (d, J = 2.9 Hz), 81.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.7; IR (neat) 3295, 2108, 1605, 1474, 1270, 1254, 1096, 767 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_9F$ 196.0688, found 196,0688.

General Procedure for the Synthesis of Fluorenes via Rh-Catalyzed Denitrogenative Cyclization. Toluene (3.0 mL) was added to a mixture of $Rh_2(esp)_2$ (1.0 mol %) and 4-(biaryl-2-yl)-1-sulfonyl-1*H*-1,2,3-triazoles **1** (0.3 mmol) in an oven-dried test tube equipped with a stir bar. The mixture was stirred for 2 h at 80 °C until **1** was completely consumed by TLC monitoring. Then, the solvent

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was removed under reduced pressure and the residue was purified via silica gel flash column chromatography to give the product **2** (85–99%; obtained as a mixture of *E* and *Z* isomers, spectral data given for the isomer mixtures) as a solid.

*N-((9H-Fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2a**):* 103 mg (99%); R_f = 0.5 (acetone/hexane =1:3); white solid; mp 154–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.78–7.76 (m, 1H), 7.71–7.69 (m, 1H), 7.63–7.60 (m, 1H), 7.54–7.52 (m, 1H), 7.41–7.29 (m, 8H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 144.8, 140.0, 138.3, 137.7, 136.8, 135.0, 130.3, 127.7, 127.1, 127.08, 127.01, 126.95, 122.7, 121.5, 120.5, 119.9, 119.0, 118.2, 21.7; IR (neat) 3316, 3063, 1650, 1448, 1406, 1354, 1335, 1206, 1165, 1083 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{17}NO_2S$ 347.0980, found 347.0980.

*N-((9H-Fluoren-9-ylidene)methyl)-4-methoxybenzenesulfonamide (**2b**):* 104 mg (95%); R_f = 0.3 (acetone/hexane = 1:3); white solid; mp 137–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 6.5 Hz, 1H), 7.72–7.70 (m, 1H), 7.64–7.61 (m, 1H), 7.52 (d, J = 6.8 Hz, 1H), 7.42–7.27 (m, 6H), 6.98 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.7, 140.0, 138.4, 137.7, 135.1, 131.3, 129.2, 127.7, 127.1, 127.0, 122.8, 121.6, 120.5, 120.0, 119.0, 118.1, 114.9, 55.8; IR (neat) 3317, 3063, 2968, 2943, 1650, 1595, 1498, 1448, 1407, 1355, 1335, 1160, 1092, 1085 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{17}NO_3S$ 363.0926, found 363.0927.

*N-((9H-Fluoren-9-ylidene)methyl)-4-chlorobenzenesulfonamide (**2c**):* 101 mg (92%); R_f = 0.4 (acetone/hexane = 1:3); yellow solid; mp 164–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 2H), 7.78 (d, J = 6.8 Hz, 1H), 7.72–7.70 (m, 1H), 7.63–7.61 (m, 1H), 7.52–7.49 (m, 3H), 7.40–7.28 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.4, 140.2, 138.2, 138.1, 138.0, 134.9, 130.0, 128.3, 127.9, 127.3, 127.2, 127.1, 122.9, 120.61, 120.60, 120.0, 119.2, 119.1; IR (neat) 3321, 3063, 2925, 1650, 1475, 1448, 1406, 1356, 1167, 1093, 1082 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{14}ClNO_2S$ 367.0434, found 367.0432.

*N-((9H-Fluoren-9-ylidene)methyl)methanesulfonamide (**2d**):* 81 mg (99%); R_f = 0.3 (acetone/hexane = 1:3); yellow solid; mp 199–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 1H), 7.76–7.74 (m, 1H), 7.66–7.64 (m, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.42–7.26 (m, 6H), 3.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.3, 138.2, 137.9, 135.0, 127.9, 127.29, 127.26, 127.21, 122.9, 121.0, 120.7, 120.0, 119.1, 118.5, 42.4; IR (neat) 3315, 3063, 2922, 1650, 1448, 1354, 1342, 1164, 1088 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{13}NO_2S$ 271.0667, found 271.0669.

*N-((9H-Fluoren-9-ylidene)methyl)propane-2-sulfonamide (**2e**):* 88 mg (98%); R_f = 0.3 (acetone/hexane = 1:3); white solid; mp 105–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 1H), 7.77–7.74 (m, 1H), 7.66–7.63 (m, 1H), 7.61–7.58 (m, 1H), 7.43–7.36 (m, 3H), 7.35–7.28 (m, 2H), 7.13 (s, 1H), 3.44 (septet, J = 6.8 Hz, 1H), 1.49 (d, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.1, 138.4, 137.8, 135.1, 127.7, 127.2, 127.0, 122.7, 122.4, 120.6, 120.0, 119.0, 117.4, 55.8, 16.8; IR (neat) 3315, 3063, 2981, 2937, 1650, 1448, 1405, 1353, 1329, 1285, 1207, 1169, 1147, 1125 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{17}NO_2S$ 299.0980, found 299.0980.

*N-((2-tert-Butyl-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2f**):* 119 mg (98%); R_f = 0.5 (acetone/hexane = 1:3); white solid; mp 168–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 3H, major + minor product), 7.71 (d, J = 7.0 Hz, 2H, minor product), 7.67–7.60 (m, 6H, major + minor product), 7.59–7.57 (m, 1H, minor product), 7.54–7.49 (m, 6H, major + minor product), 7.45–7.32 (m, 7H, major + minor product), 7.31–7.23 (m, 11H, major + minor product), 2.366 (s, 6H, major product), 2.361 (s, 3H, minor product), 1.38 (s, 18H, major product), 1.36 (s, 9H, minor product); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.55, 150.50, 144.73, 144.70, 140.1, 138.5, 138.2, 137.9, 137.7, 137.0, 136.9, 135.4, 135.3, 135.2, 130.32, 130.31, 127.6, 127.0, 126.9, 126.6, 125.2, 124.6, 122.8, 120.9, 120.8, 120.2, 120.0, 119.7, 119.5, 119.0, 118.8, 115.7, 35.19, 35.12, 31.74, 31.71, 21.7; IR (neat) 3317, 3064, 2962, 2868, 1650, 1454, 1400, 1341, 1204, 1166, 1090 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{25}NO_2S$ 403.1606, found 403.1603.

*N-((2-Methoxy-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2g**):* 96 mg (85%); R_f = 0.3 (acetone/hexane = 1:3); pale yellow solid; mp 137–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 4.6H, major + minor product) 7.64–7.48 (m, 9.2H, major + minor product), 7.38 (d, J = 5.6 Hz, 1.3H major product), 7.35 (d, J = 5.7 Hz, 1H, minor product) 7.30–7.27 (m, 5.6H, major + minor product), 7.25–7.23 (m, 1.3H, major product), 7.20 (t, J = 7.4 Hz, 2.3H, major + minor product), 7.11 (d, J = 2.2 Hz, 1.3H, major product), 7.08 (d, J = 1.6 Hz, 1H, minor product), 6.89–6.83 (m, 2.3H, major + minor product), 3.87 (s, 3.9H, major product), 3.83 (s, 3H, minor product), 2.369 (s, 3.9H, major product), 2.363 (s, 3H, minor product); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 159.3, 144.73, 144.70, 140.0, 138.2, 137.8, 136.8, 136.4, 134.8, 133.2, 131.1, 130.26, 130.24, 127.6, 126.98, 126.89, 126.88, 125.94, 125.90, 122.7, 121.4, 121.3, 120.9, 120.7, 119.5, 119.1, 118.8, 118.4, 118.3, 113.6, 112.4, 109.9, 104.1, 55.9, 55.7, 21.6; IR (neat) 3314, 3060, 2925, 1650, 1609, 1459, 1405, 1346, 1282, 1205, 1163, 1086 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}NO_3S$ 377.1086, found 377.1086.

*N-((2-Chloro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2h**):* 110 mg (96%); R_f = 0.3 (acetone/hexane =1:3); ivory solid; mp 156–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 4.8H, major + minor product), 7.74–7.72 (m, 1.4H, major product), 7.67–7.65 (m, 1.4H, major product), 7.61–7.59 (m, 2.4H, major + minor product), 7.55 (d, J = 1.6 Hz, 1.4H, major product), 7.52–7.50 (m, 1.4H, major product), 7.48–7.42 (m, 3.4H, major + minor product), 7.38–7.24 (m, 15H, major + minor product), 2,40 (s, 7.2H, major + minor product); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.0, 139.9, 139.0, 138.3, 136.7, 136.6, 136.3, 136.0, 134.9, 132.8, 132.6, 130.4, 127.8, 127.6, 127.3, 127.3, 127.1, 127.04, 127.01, 126.9, 122.9, 122.7, 122.5, 122.4, 121.2, 120.8, 120.5, 119.9, 119.0, 117.1, 117.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) IR (neat) 3350, 3042, 3005, 2924, 1655, 1447, 1316, 1289, 1144, 1124 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{16}ClNO_2S$ 381.0590, found 381.0588.

*4-Methyl-N-((2-(trifluoromethyl)-9H-fluoren-9-ylidene)methyl)-benzenesulfonamide (**2i**):* 120 mg (96%); R_f = 0.4 (acetone/hexane = 1:3); white solid; mp 186–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.3 Hz, 6H, major + minor product), 7.80–7.78 (m, 5H, major + minor product) 7.76–7.71 (m, 4H, major + minor product), 7.64–7.56 (m, 7H, major + minor product), 7.52 (d, J = 7.9 Hz, 2H, major product), 7.47 (d, J = 7.9 Hz, 3H, major + minor product), 7.39–7.37 (m, 4H, minor product), 7.34–7.31 (m, 8H, major product), 2.39 (s, 6H, major product), 2.38 (s, 3H, minor product); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.0, 142.9, 140.5, 139.2, 138.5, 138.4, 136.6, 136.3, 135.5, 134.9, 130.4, 128.9 (q, J = 31.7 Hz), 128.8 (q, J = 32.2 Hz), 128.2, 127.8, 127.2, 127.0, 124.6 (q, J = 272.2 Hz), 124.54 (q, J = 4.3 Hz), 124.52 (q, J = 272.5 Hz), 123.7 (q, J = 3.7 Hz), 122.9, 122.8, 121.2, 120.6, 120.3, 120.0, 119.4 (q, J = 3.6 Hz), 119.1, 117.1, 116.8, 115.9 (q, J = 3.8 Hz), 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) −61.36 (minor product), −61.70 (major product); IR (neat) 3302, 3065, 2925, 2870, 1657, 1397, 1355, 1321, 1164, 1114, 1085 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{16}F_3NO_2S$ 415.0854, found 415.0856.

*4-Methyl-N-((4-methyl-9H-fluoren-9-ylidene)methyl)benzenesulfonamide (**2j**):* 107 mg (99%); R_f = 0.4 (acetone/hexane = 1:3); pale yellow solid; mp 180–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.3 Hz, 1H), 7.86–7.82 (m, 5H), 7.65–7.63 (m, 1H), 7.56 (d, J = 7.2 Hz, 1H), 7.50–7.38 (m, 6H), 7.37–7.25 (m, 8H),7.21 (t, J = 6.5 Hz, 1H), 7.18 (t, J = 6.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.4 Hz, 1H), 2.68 (s, 3H), 2.66 (s, 3H), 2.37 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.7, 141.0, 138.75, 138.70, 138.0, 136.8, 135.8, 135.4, 133.8, 133.1, 130.3, 130.2, 129.4, 127.6, 126.9, 126.7, 126.6, 126.3, 123.6, 123.3, 122.7, 121.1, 121.0, 120.4, 118.7, 118.4, 118.3, 116.5, 21.7, 21.4, 21.2; IR (neat) 3323, 3050, 2950, 1650, 1450, 1401, 1355, 1332, 1163, 1088 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}NO_2S$ 361.1136, found 361.1135.

*4-Methyl-N-((3-methyl-9H-fluoren-9-ylidene)methyl)benzenesulfonamide and 4-Methyl-N-((1-methyl-9H-fluoren-9-ylidene)-methyl)benzenesulfonamide (**2k**):* 105 mg (97%); R_f = 0.4 (acetone/hexane = 1:3); white solid; mp 135–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.83 (m, 8H, unseperable isomer), 7.78–7.74 (m, 3H, unseperable isomer), 7.68–7.54 (m, 9H, unseperable

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isomer), 7.52−7.48 (m, 4H, unseperable isomer), 7.41−7.25 (m, 22H, unseperable isomer), 7.21 (t, J = 7.5 Hz, 2H, unseperable isomer), 7.12−7.08 (m, 4H, unseperable isomer), 2.58 (s, 6H), 2.43 (s, 3H), 2.42 (s, 3H), 2.39 (s, 6H), 2.38 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.8, 144.6, 140.2, 140.0, 139.8, 138.7, 138.3, 137.9, 137.8, 137.7, 136.9, 136.8, 136.6, 135.7, 135.5, 135.4, 132.4, 132.3, 130.4, 130.3, 130.2, 128.1, 127.9, 127.6, 127.1, 126.9, 126.6, 124.8, 122.8, 122.7, 122.5, 121.1, 120.6, 120.55, 120.51, 120.4, 120.3, 119.8, 119.0, 118.8, 118.49, 118.45, 117.9, 22.2, 21.8, 21.77, 21.7; IR (neat) 3314, 3051, 2922, 2861, 1647, 1452, 1397, 1355, 1334, 1163, 1087 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}NO_2S$ 361.1136, found 361.1140.

*N-((3-Chloro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide and N-((1-chloro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2l**):* 111 mg (97%); R_f = 0.4 (acetone/hexane = 1:3); yellow solid; mp 147−151 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 12 Hz, 1.3H, unseperable isomer), 7.90−7.84 (m, 8.2H, unseperable isomer), 7.80−7.20 (m, 43H, unseperable isomer), 2.40 (s, 12H, regio- and stereoisomer); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 144.9, 141.7, 140.3, 139.2, 138.8, 138.7, 138.3, 136.7, 136.68, 136.61, 136.5, 135.4, 133.6, 133.3, 132.7, 130.4, 130.39, 129.1, 128.3, 127.86, 127.83, 127.80, 127.7, 127.5, 127.2, 127.19, 127.11, 127.06, 127.01, 126.8, 123.5, 122.8, 122.7, 121.9, 120.8, 120.7, 120.2, 120.19, 120.10, 119.16, 118.4, 117.5, 117.4, 117.2, 21.8; IR (neat) 3307, 3063, 1649, 1597, 1447, 1402, 1355, 1205, 1164, 1086, 1034 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{16}ClNO_2S$ 381.0590, found 381.0590.

*N-((2,4-Difluoro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2m**):* 108 mg (94%); R_f = 0.4 (acetone/hexane = 1:3); white solid; mp 188−192 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.85 (m, 8.7H, major + minor product), 7.60−7.58 (m, 1H, minor product), 7.51−7.29 (m, 19.3H, major + minor product), 7.11−7.06 (m, 2.9H, major + minor product), 6.79 (td, J = 14.3, 1.8 Hz, 1H, minor product), 6.72 (td, J = 14.4, 2.0 Hz, 1.9H, major product), 2.41 (s, 8.7H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J = 245.3 Hz), 162.3 (d, J = 246.5 Hz), 158.1 (d, J = 253.6 Hz), 157.9 (d, J = 252.5 Hz), 145.1, 142.1 (d, J = 8.4 Hz), 142.0 (d, J = 8.9 Hz), 137.8, 136.57, 136.50 (d, J = 3.1 Hz), 134.5 (d, J = 1.3 Hz), 134.3 (d, J = 2.3 Hz), 132.1, 131.8, 130.4, 129.8, 128.5, 128.4 (d, J = 5.2 Hz), 128.0, 127.4, 127.03, 127.01, 126.8, 123.6, 123.5, 123.1 (d, J = 5.6 Hz), 122.4, 121.0 (d, J = 2.8 Hz), 120.9 (d, J = 2.5 Hz), 118.6, 117.4 (d, J = 1.7 Hz), 117.2 (d, J = 2.0 Hz), 106.4 (d, J = 3.5 Hz), 106.1 (d, J = 4.5 Hz), 103.3, 103.1, 102.8, 102.5, 102.3, 102.2 (d, J = 3.1 Hz), 102.0 (d, J = 3.6 Hz), 101.9, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) −111.77 (d, J = 6.7 Hz, minor product), −111.72 (d, J = 6.6 Hz, major product), −116.6 (d, J = 6.8 Hz, minor product), −115.4 (d, J = 6.0 Hz, major product); IR (neat) 3312, 3065, 1654, 1626, 1590, 1452, 1406, 1359, 1163, 1163, 1089 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{15}F_2NO_2S$ 383.0792, found 383.0792.

*(E)-N-((1,3-Dimethyl-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2n**):* 110 mg (98%); R_f = 0.5 (acetone/hexane = 1:3); white solid; mp 194−198 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H), 7.75 (dd, J = 6.5, 1.1 Hz, 1H), 7.53 (d, J = 6.8 Hz, 1H), 7.4 (d, J = 12.2 Hz, 2H), 7.34−7.30 (m, 5H), 6.91 (s, 1H), 2.53 (s, 3H), 2.39 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 139.9, 138.6, 136.7, 136.5, 135.9, 132.9, 132.0, 131.5, 130.2, 127.5, 126.98, 126.92, 123.9, 122.7, 120.7, 120.2, 118.5, 22.0, 21.7, 21.4; IR (neat) 3269, 3050, 2922, 2859, 1703, 1614, 1602, 1450, 1332, 1162, 1090 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{21}NO_2S$ 375.1293, found 375.1292.

*N-((1,3-Dichloro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2o**):* 110 mg (95%); R_f = 0.4 (acetone/hexane = 1:3); white solid; mp 247−251 °C; ^1H NMR (400 MHz, acetone-d_6): δ 9.74 (s, 1H), 8.65 (s, 1H), 8.10−8.08 (m, 1H), 8.04−8.01 (m, 1H), 7.96−7.94 (m, 3H), 7.50 (d, J = 8.6 Hz, 2H), 7.48−7.42 (m, 3H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ 145.6, 142.4, 138.0, 137.3, 136.3, 133.1, 132.4, 130.9, 129.6, 129.1, 128.6, 128.2, 127.9, 124.5, 121.5, 119.8, 117.0, 21.4; IR (neat) 3334, 1642, 1389, 1355, 1285, 1212, 1165, 1089 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{15}Cl_2NO_2S$ 415.0201, found 415.0201.

*N-((4H-Indeno[1,2-b]furan-4-ylidene)methyl)-4-methylbenzenesulfonamide (**2p**):* 73 mg (72%); R_f = 0.3 (acetone/hexane = 1:3); yellow solid; mp 189−193 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.48−7.41 (m, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.24−7.19 (m, 2H), 7.15−7.11 (m, 1H), 6.74 (d, J = 1.9 Hz, 0.95H), 6.53 (d, J = 1.8 Hz, 0.05H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 146.6, 144.7, 140.0, 136.8, 130.3, 129.2, 126.8, 124.9, 120.95, 119.97, 119.81, 116.8, 112.9, 106.2, 21.7; IR (neat) 3297, 3060, 1662, 1474, 1405, 1382, 1343, 1169, 1149, 1089 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}NO_3S$ 337.0773, found 337.0773.

*N-((4H-Indeno[1,2-b]thiophen-4-ylidene)methyl)-4-methylbenzenesulfonamide (**2q**):* 101 mg (96%); R_f = 0.4 (acetone/hexane = 1:3); yellow solid; mp 146−150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 2H, major + minor product), 7.55 (d, J = 7.4 Hz, 1H, major product), 7.48 (d, 7.6 Hz, 0.25H, minor product), 7.41−7.37 (m, 2H, major + minor product), 7.29−7.12 (m, 8H, major + minor product), 2.36 (s, 3H, major + minor product); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.79, 144.75, 144.2, 143.4, 140.2, 139.6, 138.7, 136.8, 136.7, 136.6, 134.8, 130.2, 129.9, 127.9, 127.6, 126.9, 126.89, 126.84, 125.1, 125.0, 123.1, 122.5, 120.0, 119.46, 119.41, 119.0, 118.5, 116.0, 21.6; IR (neat) 3310, 3065, 2921, 1654, 1405, 1353, 1336, 1169, 1150, 1089 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{15}NO_2S_2$ 353.0544, found 353.0542.

*4-Methyl-N-((3-methyl-9H-fluoren-9-ylidene)methyl)benzenesulfonamide (**2r**):* 103 mg (95%); R_f = 0.4 (acetone/hexane = 1:3); white solid; mp 180−184 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 4.4H, major + minor product), 7.73 (d, J = 6.9 Hz, 1H, minor product), 7.68−7.66 (m, 1.2H, major product), 7.60−7.57 (m, 2.4H, major + minor product), 7.52−7.48 (m, 3H, major + minor product), 7.41 (d, J = 7.8 Hz, 1.4H, major product), 7.34−7.29 (m, 13H, major + minor product), 7.10 (t, J = 7.68 Hz, 2.2H, major + minor product), 2.43 (s, 6.6H, major + minor product), 2.38 (s, 6.6H, major + minor product); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.7, 140.2, 140.1, 138.7, 137.9, 137.83, 137.80, 136.9, 136.8, 135.7, 135.4, 130.2, 128.1, 127.9, 127.6, 126.9, 127.6, 126.9, 122.8, 122.5, 121.1, 120.6, 120.5, 120.4, 120.3, 119.8, 119.0, 118.8, 118.48, 118.45, 21.7; IR (neat) 3340, 3065, 3040, 2953, 1650, 1448, 1397, 1339, 1280, 1165, 1149, 1090 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{19}NO_2S$ 361.1136, found 361.1136.

*N-((2-Fluoro-9H-fluoren-9-ylidene)methyl)-4-methylbenzenesulfonamide (**2s**):* 109 mg (99%); R_f = 0.3 (acetone/hexane = 1:3); pale pink solid; mp 186−190 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 5H, major + minor product), 7.69−7.57 (m, 7H, major + minor product), 7.52 (d, J = 7.3 Hz, 2.5H, major + minor product), 7.43 (d, J = 4.2 Hz, 1.5H, major product), 7.36−7.23 (m, 14H, major + minor product), 7.03 (td, J = 13.0, 2.1 Hz, 1H, minor product), 6.97 (td, J = 13.1, 2.3 Hz, 1.5H, major product), 2.39 (s, 7.5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 244.1 Hz), 162.3 (d, J = 244.2 Hz) 144.9, 140.4 (d, J = 8.9 Hz), 139.2, 138.4 (d, J = 1.3 Hz), 137.0, 136.7, 136.3 (d, J = 8.3 Hz), 136.0 (d, J = 2.1 Hz), 135.1 (d, J = 1.6 Hz), 133.8 (d, J = 2.0 Hz), 130.4, 127.8, 127.1, 127.0, 126.7, 122.8, 122.34, 122.31, 121.2 (d, J = 9.0 Hz), 121.0 (d, J = 9.0 Hz), 120.1, 119.6, 119.0, 117.7 (d, J = 3.1 Hz), 117.5 (d, J = 3.2 Hz), 114.5 (d, J = 22.9 Hz), 114.1 (d, J = 23.0 Hz), 110.2 (d, J = 24.4 Hz), 106.2 (d. J = 23.9 Hz), 21 7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.67 (minor product), −114.88 (major product); IR (neat) 3316, 3063, 2922, 1651, 1455, 1404, 1345, 1204, 1186, 1164, 1086 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{16}FNO_2S$ 365.0886, found 365.0884.

*N-((7H-Benzo[c]fluoren-7-ylidene)methyl)-4-methylbenzenesulfonamide (**2t**):* 118 mg (99%); R_f = 0.3 (acetone/hexane = 1:3); yellow solid; mp 115−119 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 8.4 Hz, 1H, minor product), 8.63 (d, J = 8.4 Hz, 2.3H, major product), 8.35 (d, J = 7.8 Hz, 2.3H, major product), 8.29 (d, J = 7.8 Hz, 1H, minor product), 7.91−7.87 (m, 8.6H, major + minor product), 7.80−7.30 (m, 37.6H, major + minor product), 7.36−7.30 (m, 9H, major + minor product), 2.38 (s, 9.9H, major + minor product); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.9, 140.9, 139.0, 138.5, 136.79, 136.76, 135.3, 133.6, 133.4, 132.8, 132.9, 130.3, 129.6, 129.5, 129.4, 129.2, 128.0, 127.8, 127.3, 127.1, 127.08, 127.00, 126.09, 126.0, 125.9, 125.1, 124.3, 123.8, 123.4, 123.0, 122.7, 122.6, 122.2, 120.5, 118.7, 118.2, 117.5, 21.7; IR (neat) 3309, 3055, 2982, 1734,

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1648, 1372, 1348, 1212, 1165, 1156, 1087 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{19}NO_2S$ 397.1136, found 397.1134.

General Procedure for Synthesis of Fluorenes via Tandem Cu-Catalyzed [3 + 2] Cycloaddition and Rh-Catalyzed Denitrogenative Cyclization in One Pot. Toluene (3.0 mL) was added to a mixture of CuTC (10 mol %), $Rh_2(esp)_2$ (1.0 mol %), 2-ethynylbiphenyl substrates **3** (0.3 mmol), and tosyl azide (0.3 mmol) in an oven-dried test tube equipped with a stir bar. The mixture was stirred for 2 h at 25 °C until **3** was completely consumed according to TLC monitoring, and then the mixture was stirred for 1 h at 80 °C. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure.

General Procedure for Synthesis of Aminomethyl Fluorenes via Hydrogenation.[18] MeOH (1.5 mL) was added to a mixture of Pd/C (10 wt %) and *N*-((9*H*-fluoren-9-ylidene)methyl)sulfonamides **2** (0.15 mmol) in an oven-dried test tube equipped with a stir bar. The atmosphere was replaced by H_2 (H_2 balloon bubbling). The mixture was stirred for 1 h at 50 °C until **2** was completely consumed by TLC monitoring. Then the resulting mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified via silica gel flash column chromatography to give the product **4** as a solid.

*N-((9H-Fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4a**):* 52 mg (99%); R_f = 0.5 (EtOAc/hexane = 1:3); white solid; mp 171−175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.40−7.36 (m, 4H), 7.26−7.21 (m, 4H), 4.16 (t, J = 5.8 Hz, 1H), 4.07 (t, J = 5.4 Hz, 1H), 3.53 (t, J = 5.8 Hz, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.56, 143.52, 141.6, 136.6, 129.8, 128.1, 127.4, 127.2, 124.5, 120.3, 47.0, 45.4, 21.7; IR (neat) 3276, 3063, 2922, 2856, 1597, 1449, 1329, 1159, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{19}NO_2S$ 349.1136, found 349.1137.

*N-((2-tert-Butyl-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4b**):* 61 mg (99%); R_f = 0.5 (EtOAc/hexane =1:4); white solid; mp 136−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.3 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.45−7.42 (m, 2H), 7.37−7.33 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.21−7.17 (m, 1H), 4.11 (t, J = 4.8 Hz, 1H), 4.05 (t, J = 2.4 Hz, 1H), 3.62−3.51 (m, 2H), 2.41 (s, 3H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.0, 143.6, 143.5, 143.3, 141.5, 139.0, 136.7, 129.8, 127.9, 127.2, 126.9, 125.4, 124.4, 121.2, 120.1, 120.0, 46.9, 45.4, 35.1, 31.7, 21.7; IR (neat) 3282, 3064, 2962, 1598, 1455, 1414, 1329, 1160, 1093 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{27}NO_2S$ 405.1762, found 405.1765.

*N-((2-Methoxy-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4c**):* 52.4 mg (92%); R_f = 0.3 (EtOAc/hexane = 1:3); white solid; mp 125−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.59 (m, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.35−7.32 (m, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 6.5 Hz, 1H), 6.92−6.89 (m, 2H), 4.21 (s, 1H), 4.01 (t, J = 5.2 Hz, 1H), 3.80 (s, 3H), 3.54−3.48 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 145.3, 143.4, 142.9, 141.5, 136.5, 134.3, 129.7, 128.0, 127.1, 126.2, 124.3, 121.0, 119.5, 114.0, 110.1, 55.6, 46.9, 45.4, 21.6; IR (neat) 3275, 2924, 1610, 1492, 1458, 1327, 1264, 1160, 1093, 1040 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}NO_3S$ 379.1242, found 379.1242.

*4-Methyl-N-((2-(trifluoromethyl)-9H-fluoren-9-yl)methyl)-benzenesulfonamide (**4d**):* 62 mg (99%); R_f = 0.4 (EtOAc/hexane = 1:3); white solid; mp 158−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, J = 7.6 Hz, 2H), 7.64−7.55 (m, 4H), 7.49 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 8.2 Hz, 2H), 4.33 (t, J = 6.2 Hz, 1H), 4.11 (t, J = 5.4 Hz, 1H), 3.61−3.47 (m, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.9, 144.1, 144.0, 143.8, 140.0, 136.3, 129.8, 129.1 (q, J = 32.2 Hz), 128.6, 128.4, 127.1, 125.4 (q, J = 3.8 Hz), 124.7, 124.4 (q, J = 272.2 Hz), 121.4 (q, J = 3.8 Hz), 121.0, 120.3, 47.1, 45.1, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −61.69; IR (neat) 3278, 3063, 2925, 1620, 1427, 1328, 1280, 1158, 1120, 1093 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{18}F_3NO_2S$ 417.1010, found 417.1007.

*4-Methyl-N-((4-methyl-9H-fluoren-9-yl)methyl)benzenesulfonamide (**4e**):* 54 mg (99%); R_f = 0.4 (EtOAc/hexane = 1:4); white solid; mp 155−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.26−7.21 (m, 4H), 7.16−7.15 (m, 2H), 4.12 (s, 1H), 4.12 (t, J = 5.1 Hz, 1H), 4.04 (t, J = 5.7 Hz, 2H), 2.70 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 143.7, 143.5, 142.5, 139.6, 136.5, 133.5, 130.4, 129.7, 127.9, 127.2, 127.1, 126.7, 124.3, 123.5, 121.8, 46.7, 45.6, 21.6, 21.1; IR (neat) 3279, 3041, 2923, 2857, 1598, 1454, 1420, 1330, 1159, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}NO_2S$ 363.1293, found 363.1293.

*4-Methyl-N-((1-methyl-9H-fluoren-9-yl)methyl)benzenesulfonamide (minor product) and 4-methyl-N-((3-methyl-9H-fluoren-9-yl)methyl)benzenesulfonamide (major product) (**4f**):* 53 mg (95%); R_f = 0.4 (EtOAc/hexane = 1:4); white solid; mp 130−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 2.2H, major + minor product), 7.56−7.51 (m, 4.4H, major + minor product), 7.45 (d, J = 8.2 Hz, 2.2H, major + minor product), 7.38−7.32 (m, 4.4H, major + minor product), 7.29−7.24 (m, 2.2H, major + minor product), 7.23−7.15 (m, 6.6H, major + minor product), 7.05−6.99 (m, 2.2H, major + minor product), 4.33 (t, J = 6.2 Hz, 1.2H, major product), 4.08 (dd, J = 5.4, 3.5 Hz, 1H, minor product), 4.04 (t, J = 6.0 Hz, 1H, minor product), 3.99 (t, J = 5.4 Hz, 1.2H, major product), 3.75−3.70 (m, 1H, minor product), 3.45 (quintet, J = 6.1 Hz, 3.4H, major + minor product), 2.41 (s, 3.6H, major product), 2.39 (s, 6.6H, major + minor product), 2.27 (s, 3H, minor product); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 143.7, 143.4, 143.3, 141.7, 141.6, 141.5, 140.9, 140.6, 137.7, 136.5, 136.4, 134.7, 129.7, 129.6, 129.2, 128.2, 127.97, 127.91, 127.3, 127.2, 127.15, 127.10, 124.4, 124.2, 124.1, 120.8, 120.1, 117.8, 46.64, 46.61, 45.5, 43.6, 21.65, 21.62, 18.9; IR (neat) 3279, 3042, 2921, 1597, 1452, 1418, 1330, 1160, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}NO_2S$ 363.1293, found 363.1293.

*N-((3-Chloro-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (major product) (**4ga**):* 26 mg (45%); R_f = 0.3 (EtOAc/hexane = 1:4); ivory solid; mp 128−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 1.8 Hz, 1H), 7.54 (d, J = 8.2 Hz, 2H), 7.42−7,37 (m, 2H), 7.30−7.26 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (dd, J = 8.0, 1.9 Hz, 1H), 4.32 (s, 1H), 4.02 (t, J = 5.3 Hz, 1H), 3.55−3.45 (m, 2H), 2.43 (s, 3H) ; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 143.6, 143.2, 141.9, 140.4, 136.5, 134.1, 129.8, 128.3, 128.1, 127.24, 127.09, 125.5, 124.6, 120.57, 120.26, 46.8, 45.3, 21.7; IR (neat) 3280, 3263, 2924, 2869, 1599, 1474, 1445, 1413, 1329, 1093, 1075 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{18}ClNO_2S$ 383.0747, found 383.0745.

*N-((1-Chloro-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (minor product) (**4gb**):* 21.5 mg (37%); R_f = 0.3 (EtOAc/hexane = 1:4); white solid; mp 145−150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.33−7.27 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 4.19 (t, J = 4.3 Hz, 1H), 3.98 (s, 1H), 3.88−3.75 (m, 2H), 2.41(s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 114.0, 143.5, 143.4, 140.7, 140.0, 136.5, 131.5, 129.7, 128.3, 128.2, 127.9, 127.2, 124.5, 120.7, 118.6, 47.5, 42.9, 21.7; IR (neat) 3275, 3060, 2923, 1599, 1569, 1446, 1423, 1329, 1159, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{18}ClNO_2S$ 383.0747, found 383.0744.

*N-((2,4-Difluoro-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4h**):* 57 mg (99%); R_f = 0.3 ($EtOAc/CH_2Cl_2$/hexane = 1:1:5); white solid; mp 173−177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.41−7.37 (m, 2H), 7.28−7.23 (m, 3H), 6.87 (dd, J = 7.9, 1.4 Hz, 1H), 6.79 (td, J = 14.3, 2.0 Hz, 1H), 4.37 (t, J = 6.3 Hz, 1H), 4.08 (t, J = 5.3 Hz, 1H), 3.50 (t, J = 5.9 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4 (dd, J = 248.8, 10.7 Hz), 157.9 (dd, J = 253.2, 12.6 Hz), 147.6 (dd, J = 9.5, 7.3 Hz), 143.8, 142.6 (d, J = 1.8 Hz), 138.1 (d, J = 2.9 Hz), 136.3, 129.8, 128.5, 127.3, 127.1, 124.9 (dd, J = 15.0, 3.0 Hz), 124.2, 123.3 (d, J = 5.6 Hz), 108.1 (dd, J = 23.0, 3.8 Hz), 103.5 (dd, J = 26.5, 24.1 Hz), 47.9, 45.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) −110.75 (d, J = 7.5 Hz), −116.06 (d, J = 8.1 Hz); IR (neat) 3279, 3064, 2925, 1631, 1596, 1450, 1328, 1159, 1115, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{17}F_2NO_2S$ 385.0948, found 385.0944.

*N-((1,3-Dimethyl-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4i**):* 56 mg (99%); R_f = 0.4 (EtOAc/hexane = 1:3); white

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solid; mp 158−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.37−7.33 (m, 3H), 7.21−7.16 (m, 3H), 6.83 (s, 1H), 4.06 (t, J = 4.2 Hz, 1H), 3.89 (t, J = 5.9 Hz, 1H), 3.72 (dq, J = 12.6, 3.1 Hz, 1H), 3.50 (dt, J = 12.1, 6.0 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 143.3, 141.9, 141.8, 138.1, 138.0, 136.5, 134.4, 130.2, 129.6, 127.9, 127.2, 127.1, 124.1, 120.2, 118.5, 46.3, 43.7, 21.6, 21.5, 18.9; IR (neat) 3282, 3038, 2920, 1613, 1598, 1453, 1404, 1329, 1159, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{23}NO_2S$ 377.1449, found 377.1447.

*N-((7H-Benzo[c]fluoren-7-yl)methyl)-4-methylbenzenesulfonamide (**4j**):* 59 mg (99%); R_f = 0.3 (EtOAc/hexane = 1:3); white solid; mp 196−200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.66 (t, J = 8.3 Hz, 1H), 7.57−7.45 (m, 6H), 7.29 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 4.13 (t, J = 4.8 Hz, 1H), 4.06 (t, J = 6.0 Hz, 1H), 3.69−3.66 (m, 2H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.4, 143.4, 142.7, 142.3, 136.5, 136.3, 134.0, 129.6, 129.5, 129.3, 128.5, 128.2, 127.08, 127.02, 126.5, 125.7, 124.2, 123.8, 123.3, 121.9, 47.2, 45.0, 21.6; IR (neat) 3278, 3046, 2921, 1598, 1412, 1328, 1186, 1159, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{21}NO_2S$ 399.1293, found 399,1292.

*N-((4H-Indeno[1,2-b]thiophene-4-yl)methyl)-4-methylbenzenesulfonamide (**4k**):* 50 mg (93%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1:1:5); white solid; mp 160−164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 8.3 Hz, 2H), 7.30−7.23 (m, 3H), 7.11 (td, J = 11.3, 0.9 Hz, 1H), 7.02 (d, J = 4.8 Hz, 1H), 4.52 (s, 1H), 3.91 (t, J = 6.1 Hz, 1H), 3.51 (quintet, J = 6.1 Hz, 1H), 3.27 (quintet, J = 6.4 Hz, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.1, 146.3, 143.7, 143.6, 138.5, 136.6, 129.8, 128.02, 128.01, 127.1, 125.4, 124.4, 122.3, 119.2, 45.09, 45.05, 21.6; IR (neat) 3269, 3050, 2922, 1598, 1457, 1325, 1158, 1092 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{17}NO_2S_2$ 355.0701, found 355.0701.

*4-Methyl-N-((3-methyl-9H-fluoren-9-yl)methyl)benzenesulfonamide (**4l**):* 54 mg (99%); R_f = 0.5 (EtOAc/hexane = 1:3); white solid; mp 154−158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.1 Hz, 1H), 7.55 (d, J = 8.4 Hz, 3H), 7.37 (t, J = 7.1 Hz, 2H), 7.28−7.21 (m. 4H), 7.05 (d, J = 7.6 Hz, 1H), 4.16 (t, J = 6.1 Hz, 1H), 4.02 (t, J = 5.2 Hz, 1H), 3.50 (t, J = 5.6 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 143.4, 141.63, 141.55, 140.6, 137.8, 136.6, 129.7, 128.3, 127.9, 127.24, 127.17, 124.4, 124.1, 120.9, 120.1, 46.6, 45.6, 21.66, 21.64; IR (neat) 3286, 3032, 2915, 1597, 1439, 1403, 1331, 1153, 1079 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}NO_2S$ 363.1293, found 363.1293.

*N-((2-Fluoro-9H-fluoren-9-yl)methyl)-4-methylbenzenesulfonamide (**4m**):* 55 mg (99%); R_f = 0.6 (acetone/hexane = 1:2); white solid; mp 183−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.63 (m, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.42−7.37 (m, 2H), 7.27−7.23 (m, 3H), 7.05 (td, J = 13.1, 2.4 Hz, 1H), 6.99 (dd, J = 8.6, 2.2 Hz, 1H), 4.15 (t, J = 6.2 Hz, 1H), 4.05 (t, J = 5.2 Hz, 1H), 3.59−3.47 (m, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J = 246.3 Hz), 145.7 (d, J = 8.3 Hz), 143.7, 143.17 (d, J = 2.0 Hz), 140.8, 137.5 (d, J = 2.4 Hz), 136.3, 129.8, 128.3, 127.20, 127.16, 124.4, 121.2 (d, J = 8.9 Hz), 120.1, 115.1 (d, J = 23.0 Hz), 112.0 (d, J = 23.1 Hz), 47.0 (d, J = 2.3 Hz), 45.2, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.06; IR (neat) 3267, 3055, 2924, 1589, 1488, 1454, 1325, 1157, 1088 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{18}FNO_2S$ 367.1042, found 367.1042.

General Procedure for Synthesis of Aminomethyl Fluorenes via Rh-Catalyzed Denitrogenative Cyclization Followed by Reduction in One Pot.[19] Toluene (3.0 mL) was added to a mixture of $Rh_2(esp)_2$ (1.0 mol %) and 4-(biaryl-2-yl)-1-sulfonyl-1*H*-1,2,3-triazole **1** (0.3 mmol) in oven-dried test tube equipped with a stir bar. The mixture was stirred for 2 h at 80 °C until **1** was completely consumed according to TLC monitoring. After the mixture was cooled to room temperature, $NaBH_3CN$ (0.6 mmol) was added, and the mixture was further stirred at 80 °C for 12 h. Then, the resulting mixture was diluted with CH_2Cl_2 after cooling to room temperature and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the residue was purified via silica gel flash column chromatography to give the product **4** as a solid.

*N-((9H-Fluoren-9-yl)methyl)-4-chlorobenzenesulfonamide (**4n**):* 91 mg (82%); R_f = 0.4 (EtOAc/hexane = 1:4); white solid; mp 151−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.38−7.31 (m, 6H), 7.24−7.20 (m, 2H), 4.29 (s, 1H), 4.03 (t, J = 4.8 Hz, 1H), 3.58 (t, J = 5.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.1, 141.5, 139.0, 138.0, 129.3, 128.4, 128.1, 127.4, 124.3, 120.3, 46.9, 45.2; IR (neat) 3279, 1586, 1476, 1449, 1396, 1333, 1163, 1094 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{16}ClNO_2S$ 369.0590, found 369.0590.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data (**2a**) (CIF) and ^{1}H, ^{13}C{^{1}H}, ^{19}F, NOE, and HSQC NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor Choong Eui Song (Sungkyunkwan University) on the occasion of his 60th birthday.

■ REFERENCES

(1) (a) Harvey, R. G. *Polycyclic Aromatic Hydrocarbons*; Wiley-VCH: New York, 1996. (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (c) Watson, M. D.; Fethtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267. (d) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891. (e) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (f) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (g) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

(2) (a) Mo, Y.; Jiang, X.; Cao, D. *Org. Lett.* **2007**, *9*, 4371. (b) Yeh, H.-C.; Chien, C.-H.; Shih, P.-I.; Yuan, M.-C.; Shu, C.-F. *Macromolecules* **2008**, *41*, 3801. (c) Aly, S. M.; Ho, C.-L.; Wong, W.-Y.; Fortin, D.; Harvey, P. D. *Macromolecules* **2009**, *42*, 6902. (d) Pu, K.-Y.; Zhan, R.; Liu, B. *Chem. Commun.* **2010**, *46*, 1470. (e) Zafra, J. L.; Casado, J.; Perepichka, I. I.; Perepichka, I. F.; Bryce, M. R.; Ramirez, F. J.; Navarrete, J. T. L. *J. Chem. Phys.* **2011**, *134*, 044520. (f) Zhu, M.; Ye, T.; Li, C.-G.; Cao, X.; Zhong, C.; Ma, D.; Qin, J.; Yang, C. *J. Phys. Chem. C* **2011**, *115*, 17965.

(3) (a) Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1988**, *110*, 1862. (b) Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett.* **2002**, *4*, 2157. (c) Campeau, L.-C.; Parisien, M.; Jean, A.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 581. (d) Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 1434. (e) Dong, C.-G.; Hu, Q.-S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2289. (f) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760. (g) Wang, F.; Ueda, W. *Chem. Commun.* **2008**, 3196. (h) Hwang, S. J.; Kim, H. J.; Chang, S. *Org. Lett.* **2009**, *11*, 4588.

(4) Kirmse, W.; Kund, K.; Ritzer, E.; Dorigo, A. E.; Houk, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6045.

(5) Kim, J.; Ohk, Y.; Park, S. H.; Jung, Y.; Chang, S. *Chem.—Asian J.* **2011**, *6*, 2040.

DOI: 10.1021/jo5027113
J. Org. Chem. 2015, 80, 722−732

(6) Wang, Y.; McGonigal, P. R.; Herle, B.; Besora, M.; Echavarren, A. M. *J. Am. Chem. Soc.* **2014**, *136*, 801.
(7) Morimoto, K.; Itoh, M.; Hirano, K.; Satoh, T.; Shibata, Y.; Tanaka, K.; Miura, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5359.
(8) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910.
(9) Liu, T.-P.; Xing, C.-H.; Hu, Q.-S. *Angew. Chem., Int. Ed.* **2010**, *49*, 2909.
(10) (a) Chernyak, N.; Gevorgyan, V. *Adv. Synth. Catal.* **2009**, *351*, 1101. (b) Chernyak, N.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 5636.
(11) (a) Hirano, M.; Kawazu, S.; Komine, N. *Organometallics* **2014**, *33*, 1921. (b) Gorin, D. J.; Watson, L. D. G.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 3736. (c) Yang, J.-S.; Lee, Y.-R.; Yan, J.-L.; Lu, M.-C. *Org. Lett.* **2006**, *8*, 5813.
(12) For reviews, see: (a) Chattopadhyay, B.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 862. (b) Davies, H. M. L.; Alford, J. S. *Chem. Soc. Rev.* **2014**, *43*, 5151. (c) Anbarasan, P.; Yadagiri, D.; Rajasekar, S. *Synthesis* **2014**, *46*, 3004 and references therein. (d) Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 14972. (e) Miura, T.; Yamauchi, M.; Murakami, M. *Chem. Commun.* **2009**, 1470. (f) Chattopadhyay, B.; Gevorgyan, V. *Org. Lett.* **2011**, *13*, 3746. (g) Shi, Y.; Gevorgyan, V. *Org. Lett.* **2013**, *15*, 5394. (h) Miura, T.; Hiraga, K.; Biyajima, T.; Nakamuro, T.; Murakami, M. *Org. Lett.* **2013**, *15*, 3298. (i) Schultz, E. E.; Sarpong, R. *J. Am. Chem. Soc.* **2013**, *135*, 4696. (j) Chuprakov, S.; Kwok, S. W.; Fokin, V. V. *J. Am. Chem. Soc.* **2013**, *135*, 4652. (k) Parr, B. T.; Green, S. A.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 4716. (l) Zibinsky, M.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1507. (m) Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6802. (n) Miura, T.; Funakoshi, Y.; Murakami, M. *J. Am. Chem. Soc.* **2014**, *136*, 2272. (o) Kwok, S. W.; Zhang, L.; Grimster, N. P.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 3452. (p) Zibinsky, M.; Fokin, V. V. *Org. Lett.* **2011**, *13*, 4870. (q) Alford, J. S.; Spangler, J. E.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 11712. (r) Jeon, H. J.; Jung, D. J.; Kim, J. H.; Kim, Y.; Bouffard, J.; Lee, S.-g. *J. Org. Chem.* **2014**, *79*, 9865. (s) Jung, D. J.; Jeon, H. J.; Kim, J. H.; Kim, Y.; Lee, S.-g. *Org. Lett.* **2014**, *16*, 2208. (t) Bae, I.; Han, H.; Chang, S. *J. Am. Chem. Soc.* **2005**, *127*, 2038. (u) Gulevich, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2013**, *52*, 1371. (v) Tang, X.-Y.; Zhang, Y.-S.; He, L.; Wei, Y.; Shi, M. *Chem. Commun.* **2015**, *51*, 133.
(13) (a) Kim, C.-E.; Park, S.; Eom, D.; Seo, B.; Lee, P. H. *Org. Lett.* **2014**, *16*, 1900. (b) Park, S.; Yong, W.-S.; Kim, S.; Lee, P. H. *Org. Lett.* **2014**, *16*, 4468. (c) Kim, S.; Mo, J.; Kim, J.; Ryu, T.; Lee, P. H. *Asian J. Org. Chem.* **2014**, *3*, 926. (d) Kim, C.-E.; Park, Y.; Park, S.; Lee, P. H. *Adv. Synth. Catal.* **2014**, DOI: 10.1002/adsc.201400604.
(14) (a) Yoo, E. J.; Ahlquist, M.; Kim, S. H.; Bae, I.; Fokin, V. V.; Sharpless, K. B.; Chang, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 1730. (b) Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952. (c) Liu, Y.; Wang, X.; Xu, J.; Zhang, Q.; Zhao, Y.; Hu, Y. *Tetrahedron* **2011**, *67*, 6294.
(15) (a) Grünanger, P.; Finzi, P. V. *Tetrahedron Lett.* **1963**, *4*, 1839. (b) Harmon, R. E.; Stanley, F., Jr.; Gupta, S. K.; Johnson, J. *J. Org. Chem.* **1970**, *35*, 3444. (c) Mckinney, M. A.; Patel, P. P. *J. Org. Chem.* **1973**, *38*, 4059. (d) Himbert, G.; Frank, D.; Regit, M. *Chem. Ber.* **1976**, *109*, 370. (e) Kwok, S. W.; Zhang, L.; Grimster, N. P.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2014**, *53*, 3452.
(16) (a) Odedra, A.; Wu, C.-J.; Pratap, T. B.; Huang, C.-W.; Ran, Y.-F.; Liu, R.-S. *J. Am. Chem. Soc.* **2005**, *127*, 3406. (b) Wang, H.-L.; Hu, H. Z.; Zhou, A.-X.; Yang, S.-D. *Org. Lett.* **2013**, *15*, 5302.
(17) (a) Jackson, T. J.; Herndon, J. W. *Tetrahedron* **2001**, *57*, 3859. (b) Hossain, M. L.; Ye, F.; Liu, Z.; Xia, Y.; Shi, Y.; Zhou, L.; Zhang, Y.; Wang, J. *J. Org. Chem.* **2014**, *79*, 8689.
(18) Sajiki, H.; Ikawa, T.; Hirota, K. *Org. Process Res. Dev.* **2005**, *9*, 219.
(19) Yang, J.-M.; Zhu, C.-Z.; Tang, X.-Y.; Min, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 5142.

DOI: 10.1021/jo5027113
J. Org. Chem. 2015, 80, 722−732