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Synthesis of Functionalized 9-Substituted Fluorene Derivatives via Boron Trifluoride Catalysed Reaction of Coplanar 9-(Phenylethynyl)-9*H*-fluoren-9-ols, Aryl Aminoamides and *N*-Bromosuccinimide

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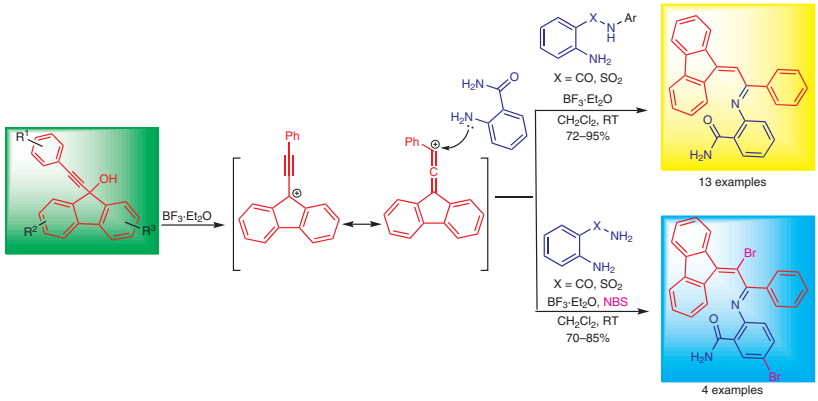

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Abstract A boron trifluoride catalysed reaction of coplanar 9-(phenylethynyl)-9*H*-fluoren-9-ols with various 2-aminobenzamides affords a number of highly functionalized, conjugated (*Z*)-2-((2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino) benzamides in excellent yield. The reaction in the presence of *N*-bromosuccinimide affords (*E*)-5-bromo-2-((2-bromo-2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzamides in very good yields. The scope of the reaction is demonstrated by selecting *N*-aryl substituted 2-aminobenzamides and aminosulfonamides as reaction partners. The structures of representative compounds were established by single-crystal XRD analysis. Based on the structure of the products, a plausible mechanism via formation of allene carbocation intermediates is proposed.

Key words aryl aminoamides, propargylic alcohol, N-bromosuccinimide, $BF_3{\cdot}OEt_2$, fluorene, allene

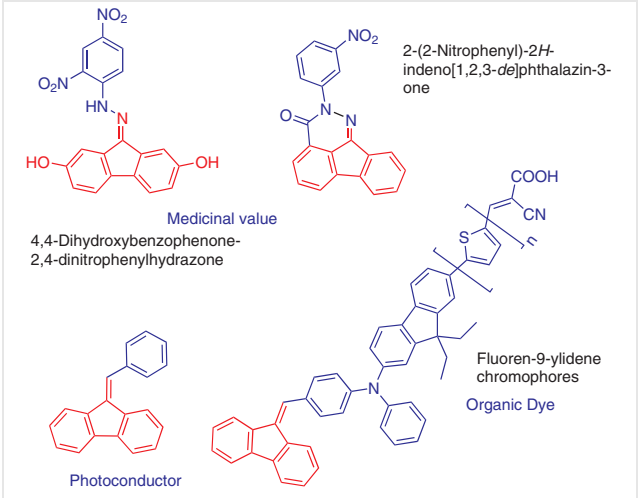


Figure 1 Selected materials and bioactive molecules based on the 9-substituted fluorene core structure

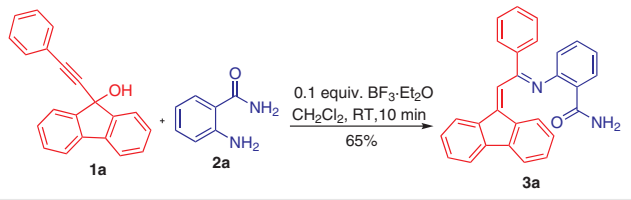
Fluorene-based compounds have been widely investigated because of their wide range of applications as organic materials,[1] semiconductors,[2] optoelectronics,[3] organic dyes,[4] photoconductors[5] as well as their applications in solar cells,[6] fuel cells,[7] and materials science[8] as indicated in Figure 1. Their highly fluorescent nature has enabled fluorene derivatives to be used in bright and efficient displays.[9]

The presence of two benzylic acidic hydrogens at the C-9 position of fluorene activates them towards alkylation under basic conditions. Compounds with a fluorene motif such as NPC 16570 and NPC 17923 have been used as anti-inflammatory agents and inhibitors of leukocytes in inflamed tissue,[10] and also exhibit anticancer activity as well as cardiac and bone marrow toxicity.[11] Propargylic alcohols and their derivatives are useful precursors in organic synthesis.[12] Propargylic alcohols react with metal salts, iodine, and Lewis acids,[13] and they undergo nucleophilic substitution reactions via allene carbocation or propargyl cation species. In these situations, the allene intermediate shows diverse reactivity as well as selectivity.[14] Aryl aminoamides have been used as starting materials for the preparation of heterocyclic compounds and aryl amino amide appended carbocycles.[15] We have utilised fluorenone for the synthesis of spirofluorene-based fluorescent molecules[16] and we have recently reported the reaction of fluorene-9-propargylic alcohols with isatin imines for the preparation of blue emissive compounds via highly stable propargylic cation

intermediates.[17] The reactions of aryl substituted propargylic alcohols with several nucleophiles such as sulfonamides,[19] nitroso compounds,[20] acetamides,[21] tosylhydrazines,[12] and imines[22] have been investigated by various research groups, to provide highly functionalized products through allenyl cation intermediates.[23] It should be noted that the two aryl groups in the diaryl substituted phenyl propargylic alcohols are conformationally orthogonal and decisive in the formation, stability, and reactivity of either carbocation or allenyl intermediate.[24] On the other hand, when the aryl groups are coplanar or nonplanar, the formation, stability, and reactivity of the reactive intermediate can be modified and provide products via the most stable intermediate. To our knowledge, the reaction of coplanar 9-(phenylethynyl)-9*H*-fluoren-9-ols with amino amides has not been reported. Thus, we have explored the reaction of rigid and coplanar diaryl substituted fluorene propargylic alcohols with substituted benzamides and sulfonamides.

In contrast to previous reports that coplanar fluorene propargylic alcohols with isatin imine nucleophiles affords products via the propargylic cation, herein we report the reaction with nucleophiles having labile amine protons, the reactivity being found to be reversed to afford products via an allenyl cation. The preliminary results of the study are presented in this manuscript.

Initially, a reaction between 1 equivalent of fluorenone propargylic alcohol **1a**[25] in dichloromethane and 1 equivalent of 2-aminobenzamide (**2a**) and 0.1 equivalents of $BF_3{\cdot}Et_2O$ at room temperature for 10 minutes afforded (*Z*)-2-((2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)-benzamide (**3a**) in 65% yield (Scheme 1, Table 1, entry 1). The structure of **3a** was established by FTIR, ^1H NMR, ^{13}C NMR, DEPT-135 and HRMS analyses.



Scheme 1 Synthesis of compound **3a**

To improve the yield and to optimize the reaction conditions for the synthesis of compound **3a**, a study was carried out, varying reaction parameters such as relative quantities and nature of the acid catalyst, solvent and reaction time. Thus, performing the reaction using 0.3 equivalent of $BF_3{\cdot}Et_2O$ led to the yield of the product **3a** being improved to 92% and was ultimately found to be optimal (Table 1, entry 2). Reactions using 0.5 equivalent of catalyst slightly decreased the yield to 89% (entry 3). Catalysts such as *p*-TsOH, $FeCl_3$, and $AlCl_3$, led to either decreased yields or no reaction (entries 4–7). Hence, $BF_3{\cdot}Et_2O$ was found to be the most suitable catalyst. Other solvents such as acetonitrile, methanol, and toluene did not improve the yield (entries 8–10). Hence, dichloromethane was found to be the most suitable solvent. An experiment without a Lewis acid catalyst failed to provide any product (entry 11).

Table 1 Optimization of Synthesis of Compound **3a**

Entry	Catalyst	Solvent	Catalyst (equiv)	Time (min)	Yield of **3a** (%)[a]
1	$BF_3{\cdot}OEt_2$	DCM	0.1	10	65
2	$BF_3{\cdot}OEt_2$	DCM	0.3	5	92[b]
3	$BF_3{\cdot}OEt_2$	DCM	0.5	5	89
4	p-TsOH	DCM	0.3	30	40
5	$FeCl_3$	DCM	0.3	30	40
6	$AlCl_3$	DCM	0.3	30	no reaction
7	$InBr_3$	DCM	0.3	7	80
8	$BF_3{\cdot}OEt_2$	MeCN	0.8	0.5	decomposition
9	$BF_3{\cdot}OEt_2$	MeOH	0.8	30	10
10	$BF_3{\cdot}OEt_2$	toluene	0.8	5	no reaction
11	–	DCM		300	no reaction

[a] Isolated yield after column purification.
[b] Optimized conditions.

Having the optimized conditions in hand, the scope of the reaction was investigated by using a number of propargylic alcohols **1a–d** and aryl aminoamides **2a–g** (Figure 2). Under the optimized conditions, all reactions proceeded well to afford the corresponding products **3a–m** in excellent yields (Table 2, Figure 3). To demonstrate the diversity of

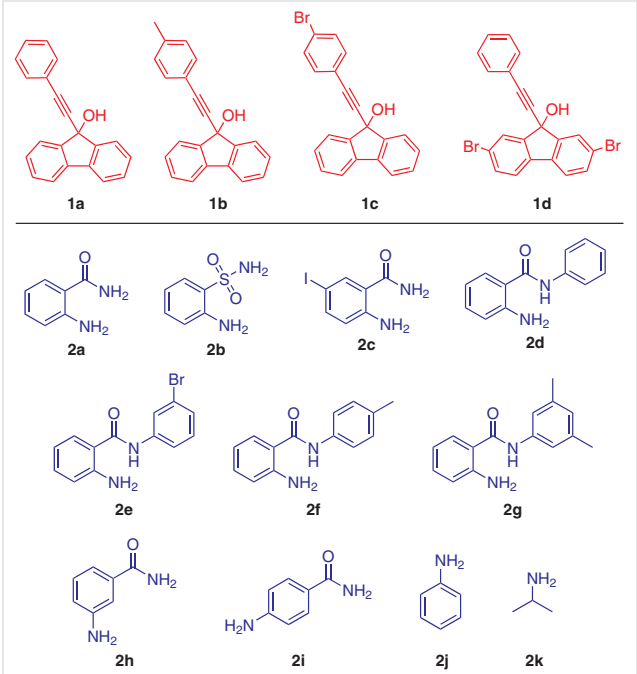


Figure 2 Various propargyl alcohols **1a–c** and aryl aminoamides **2a–k**

the amino derivatives in the reaction, 2-aminobenzenesulfonamide **2b** was reacted with propargyl alcohol **1a** to provide the sulfonamide derivative **3b** in 90% yield (entry 2). Reaction of propargylic alcohol **1a** with 5-iodobenzamide **2c** yielded product **3c** in 91% yield (entry 3). In a further exploration of various benzamides, substituted aminoamides **2d–f** were chosen to react with **1a** to afford products **3d–f** in good yields (entries 4–6). Substituted aminoamides **2d–f** were prepared from isatoic anhydride and aryl amines in water at room temperature.[26] The structure and relative stereochemistry of the representative compound **3e** was confirmed by single-crystal XRD analysis (Figure 4).[27]

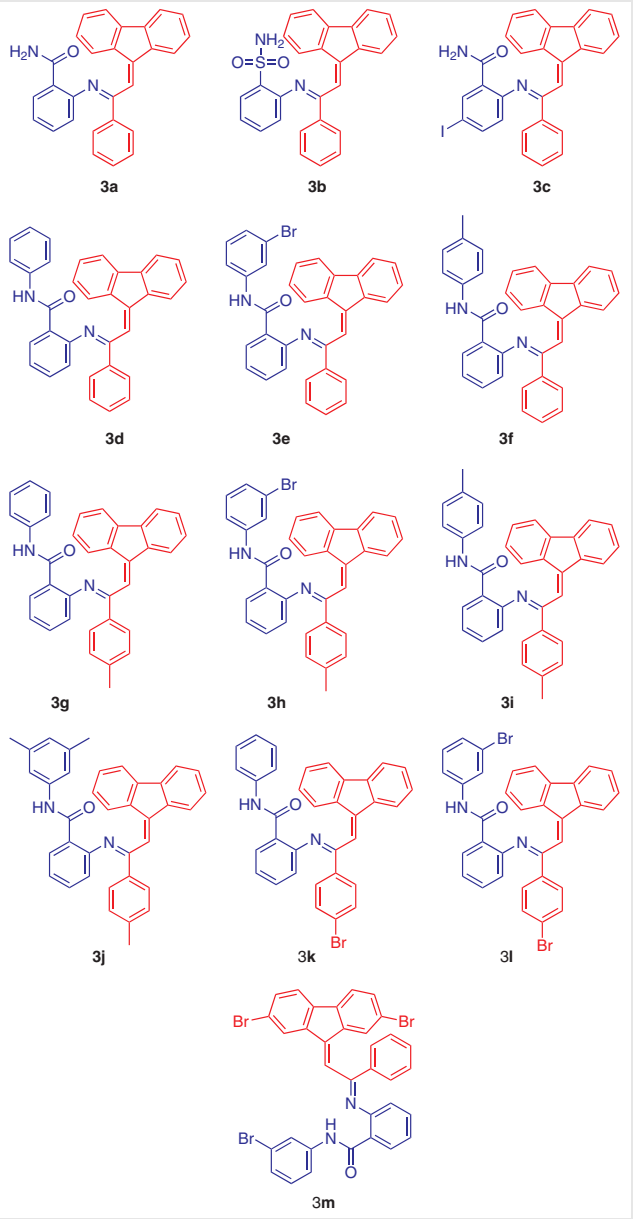


Figure 3 Synthesized compounds **3a–m**

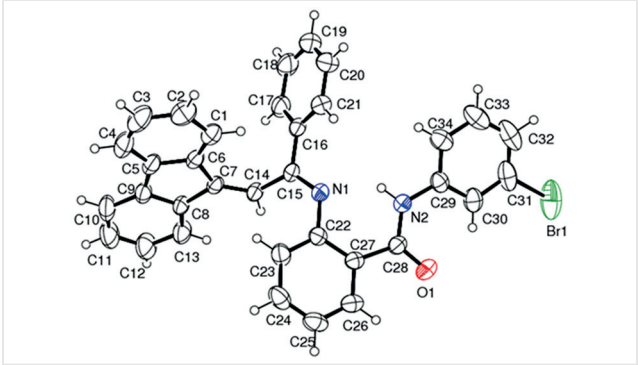


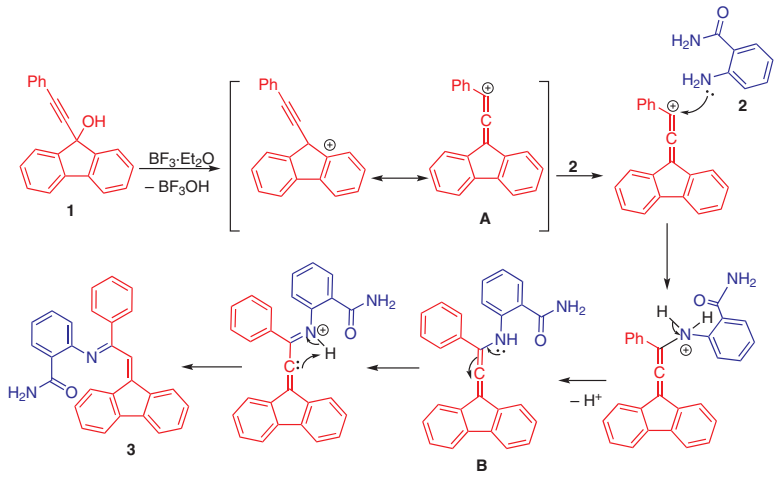
Figure 4 ORTEP diagram of compound **3e** (CCDC-1967615)[27]

To study the reactivity of fluorene propargylic alcohols bearing electron-donating groups, substrate **1b** was reacted with substituted amino amides **2d–f** to provide compounds **3g–i** in moderate to good yields (Table 2, entries 7–9). Alcohol **1b**, on reaction with dimethyl substituted amino amide **2g**, afforded product **3j** in low yield (entry 10). Furthermore, reaction of alcohol **1c** with amino amides **2d–e** proceeded smoothly to afford the respective products **3k** and **3l** (entries 11 and 12). To study the effect of substitution on the fluorenone ring, propargylic alcohol **1d** was reacted with **2e**, furnishing product **3m** in 72% yield (entry 13).

Table 2 Reaction Scope[a]

Entry	Substrate	Aminoamide	Product (Yield, %)[b]
1	**1a**	**2a**	**3a** (92)
2	**1a**	**2b**	**3b** (90)
3	**1a**	**2c**	**3c** (91)
4	**1a**	**2d**	**3d** (89)
5	**1a**	**2e**	**3e** (90)
6	**1a**	**2f**	**3f** (88)
7	**1b**	**2d**	**3g** (87)
8	**1b**	**2e**	**3h** (91)
9	**1b**	**2f**	**3i** (88)
10	**1b**	**2g**	**3j** (75)
11	**1c**	**2d**	**3k** (84)
12	**1c**	**2e**	**3l** (83)
13	**1d**	**2e**	**3m** (69)
14	**1a**	**2h**	decomposition
15	**1a**	**2i**	decomposition
16	**1a**	**2j**	decomposition
17	**1a**	**2k**	decomposition

[a] Reaction conditions: $BF_3{\cdot}Et_2O$ (0.3 equiv), CH_2Cl_2, 5 min. r.t.
[b] Isolated yield after column purification.

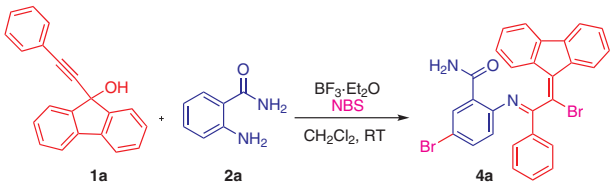


Scheme 2 Plausible mechanism for the formation of compound **3**

It is worth noting that the reaction of alcohol **1a** with *meta*-substituted aminobenzamide **2h** and *para*-substituted aminobenzamide **2i** failed to provide the expected product. Thus, the reaction occurs only with *ortho*-amino arylamides, possibly due to hydrogen bonding. On the other hand, we also wished to test the reaction with arylamines such as aniline **2j** and aliphatic amines such as isopropylamine **2k** with alcohol **1a**. However, both reactions failed to provide the desired product and decomposed.

Based on the structure of the products formed and on literature reports,[17] a plausible mechanism for the formation of product **3** is proposed in Scheme 2. Accordingly, initial reaction of the fluorene derived propargylic alcohol **1** with BF_3[12e,18] generates the propargyl cation/allenic carbocation intermediate **A**. Subsequent nucleophilic attack of the lone pair of electrons of the amine group of arylaminoamide **2** onto the allenic carbocation **A** provides allene substituted product **B**. Subsequent skeletal rearrangement of **B** leads to product **3**.

To explore the scope of the reaction further and to diversify the products with halogen derivatives, the reaction shown in Scheme 3 in the presence of *N*-bromosuccinimide (NBS) was proposed. Thus, the reaction was carried out with 1 equiv of fluorenone derived propargylic alcohol **1a** in dichloromethane, 1 equiv of 2-aminobenzamide **2a**, 1 equiv of NBS, and 0.3 equiv amount of $BF_3{\cdot}Et_2O$ at room temperature for 5 minutes to afford the dibromination product, namely, (*E*)-5-bromo-2-((2-bromo-2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzamide (**4a**) in good yield (60%; Scheme 3). The structure and relative stereochemistry of compound **4a** was confirmed by single-crystal XRD analysis (Figure 5).[27]



Scheme 3 Synthesis of compound **4a**

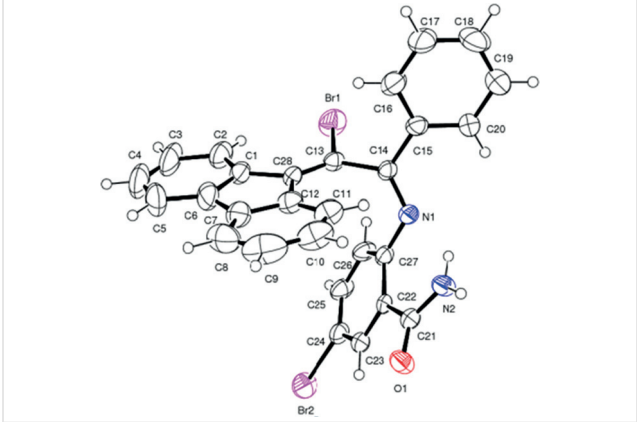


Figure 5 ORTEP diagram of compound **4a** (CCDC-1957144)[27]

Under the optimized conditions, the scope of the reaction in the presence of NBS was demonstrated by using various propargylic alcohols **1a** and **1b** and aryl benzamides **2a**, sulfonamide **2b** and iodo-substituted aryl benzamide **2c** to produce products **4a–d** in 60–75% yields (Figure 6). The structure of all the new compounds was established by spectroscopic analyses.[28]

Based on the products and on literature precedents,[17,19–22] a possible mechanism for the formation of compound **4** is shown in Scheme 4. The allenic carbocation intermediate **A** with aminobenzamide **2** forms allene intermediate **B**. Meanwhile, in the presence of $BF_3{\cdot}OEt_2$, NBS is activated and

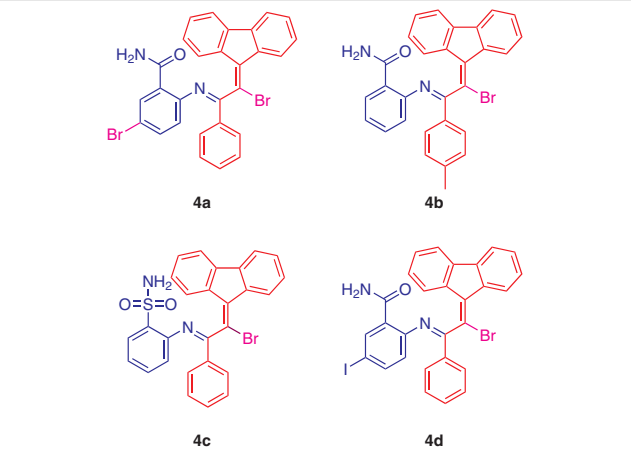


Figure 6 Synthesized compounds **4a–d**

eliminates a bromine cation. Due to the electron-donating nature of nitrogen, the electron-rich internal carbon atom of allene intermediate **B** reacts with the bromine cation to form intermediate **C**. Elimination of a proton from intermediate **C** followed by aromatic electrophilic bromination forms the observed compound **4**.

In conclusion, we have developed a procedure for the synthesis of (*Z*)-2-((2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzamides via BF_3-mediated reaction of coplanar 9-(phenylethynyl)-9*H*-fluoren-9-ols with various 2-aminobenzamides.[28] Reaction in the presence of NBS afforded (*E*)-5-bromo-2-((2-bromo-2-(9*H*-fluoren-9-ylidene)-1-ethenylethylidene)amino)benzamides. A plausible mechanism for the formation of products via an allene carbocation intermediate is proposed. The structure of representative compounds has been established by single-crystal XRD analysis.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1706015.

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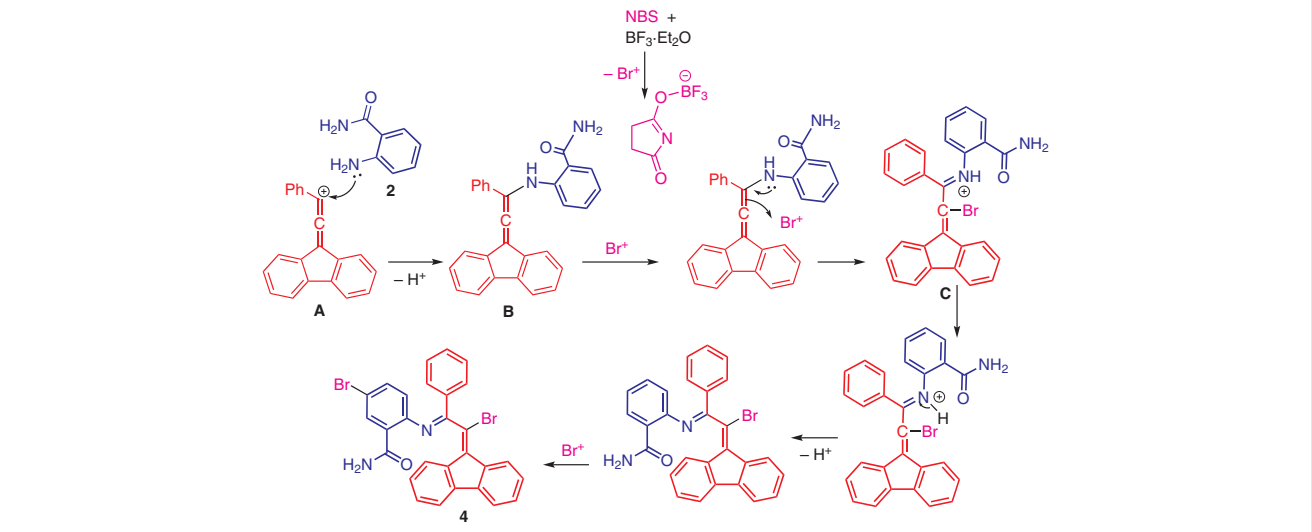

Scheme 4 Plausible mechanism for the formation of compound **4**

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(27) CCDC-1967615 (**3e**) and CCDC-1957144 (**4a**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.
(28) **Synthesis of Compounds 3a–m; General Procedure:** To a stirred solution of propargylic alcohol derivative of fluorenone **1** (0.35 mmol, 1equiv) and aminobenzamide **2** (0.35 mmol, 1 equiv) in dichloromethane (5 mL) was added $BF_3{\cdot}OEt_2$ (0.1 mmol, 0.3 equiv). The resulting reaction mixture was stirred at room temperature for 5 minutes. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with dichloromethane, washed with distilled water and saturated brine. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: hexane/EtOAc) to afford the corresponding compounds **3a–m** in good yields.
Synthesis of Compounds 4a–d; General Procedure: To a solution of propargylic alcohol **1** (0.35 mmol, 1 equiv) and aminobenzamide **2** (0.35 mmol, 1 equiv) in dichloromethane (5 mL) was added NBS (0.4 mmol, 1.2 equiv) followed by $BF_3{\cdot}Et_2O$ (0.1 mmol, 0.3 equiv) and the reaction mixture was stirred at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with dichloromethane, washed with distilled water and saturated brine. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (eluent: hexane/EtOAc) to afford the corresponding compounds **4a–d** in good yields.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-phenylethylidene)-amino)benzamide (3a): Yield: 92%; yellow solid; R_f (30% EtOAc–Hexane): 0.45. FTIR (KBr): 3293, 3057, 2922, 2852, 1914, 1810, 1656, 1611, 1487, 1447, 1378, 1289, 1267, 1236, 1158, 1107, 1016, 943, 836, 747, 730, 697, 622 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.25 (s, 1 H), 8.13 (dd, *J* = 7.5, 1.8 Hz, 1 H), 7.98–7.95 (m, 2 H), 7.58–7.53 (m, 2 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.43 (d, *J* = 7.3 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.29 (t, *J* = 7.1 Hz, 1 H), 7.21–7.15 (m, 2 H), 7.10 (ddd, *J* = 7.5, 4.8, 1.7 Hz, 3 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 6.85 (s, 1 H), 6.73 (dd, *J* = 7.6, 1.3 Hz, 1 H), 6.07 (s, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 119.1, 119.9, 120, 120.9, 121.1, 124.7, 125.7, 127.4, 127.5, 128.7, 129.2, 129.6, 129.7, 131.4, 132, 135.5, 137.3, 137.7, 139.9, 141.7, 142.7, 148.6, 166.9, 168.6. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{28}H_{21}N_2O$: 401.1653; found: 401.1652.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-phenylethylidene)-amino)benzenesulfonamide (3b): Yield: 90%; yellow solid; R_f (30% EtOAc–Hexane): 0.47. FTIR (KBr): 3360, 3268, 2923, 1918, 1643, 1604, 1587, 1535, 1445, 1401, 1344, 1276, 1254, 1209, 1171, 1128, 1070, 1024, 942, 857, 833, 807, 772, 730, 689, 620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.06–8.03 (m, 2 H), 8.00 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.66 (dd, *J* = 7.5, 0.8 Hz, 2 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.53–7.48 (m, 1 H), 7.44–7.37 (m, 3 H), 7.32 (ddd, *J* = 10.2, 8.2, 1.3 Hz, 2 H), 7.27 (dd, *J* = 2.6, 1.3 Hz, 1 H), 7.25–7.22 (m, 2 H), 7.18–7.14 (m, 1 H), 7.03 (td, *J* = 7.6, 1.1 Hz, 1 H), 6.97 (s, 1 H), 6.77 (dd, *J* = 7.9, 1.0 Hz, 1 H), 5.34 (s, 2 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 119.7, 119.9, 120.1, 120.9, 121.5, 124.6, 125.9, 127, 127.4, 127.6, 128.8, 129.2, 129.6, 129.7, 132.3, 132.8, 133.6, 135.8, 137, 137.7, 139.9, 141.9, 142.4, 148.2, 169.5. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{27}H_{21}N_2O_2S$: 437.1323; found: 437.1323.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-phenylethylidene)-amino)-5-iodobenzamide (3c): Yield: 91%; yellow solid; R_f (30% EtOAc–Hexane): 0.50. FTIR (KBr): 3413, 3339, 3149, 2971, 2924, 1670, 1608, 1575, 1495, 1447, 1404, 1350, 1294, 1256, 1211, 1159, 1095, 1018, 951, 918, 862, 813, 780, 733, 698, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.46 (d, *J* = 2.1 Hz, 1 H), 8.19 (s, 1 H), 7.99–7.94 (m, 2 H), 7.57 (dd, *J* = 11.0, 7.6 Hz, 2 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.48–7.39 (m, 2 H), 7.34 (ddd, *J* = 10.7, 8.3, 4.3 Hz, 3 H), 7.22 (ddd, *J* = 7.6, 4.3, 0.9 Hz, 2 H), 7.06 (d, *J* = 7.7 Hz, 1 H), 6.91 (td, *J* = 7.7, 0.9 Hz, 1 H), 6.82 (s, 1 H), 6.48 (d, *J* = 8.4 Hz, 1 H), 5.74 (s, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 89.9, 118.5, 120.0, 120.4, 121.2, 122.8, 125.8, 126.7, 127.5, 127.7, 128.8, 129.3, 129.9, 129.4, 132.4, 135.4, 137.2, 137.6, 140.1, 140.2, 140.7, 141.9, 143.2, 148.1, 166.9, 167.5. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{28}H_{20}IN_2O$: 527.0620; found: 527.0619.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-phenylethylidene)-amino)-*N*-phenylbenzamide (3d): Yield: 89%; yellow crystals; R_f (10% EtOAc–Hexane): 0.49. FTIR (KBr): 3418, 3114, 3058, 1915, 1710, 1662, 1595, 1537, 1494, 1445, 1401, 1315, 1279, 1249, 1157, 1124, 882, 752, 730, 694, 620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.75 (s, 1 H), 8.25–8.20 (m, 1 H), 8.05–8.01 (m, 2 H), 7.52 (dd, *J* = 12.3, 7.5 Hz, 2 H), 7.47–7.36 (m, 6 H), 7.26 (dd, *J* = 7.5, 0.8 Hz, 1 H), 7.17 (d, *J* = 2.3 Hz, 1 H), 7.15–7.11 (m, 5 H), 7.08–7.06 (m, 1 H), 6.96–6.92 (m, 1 H), 6.90 (s, 1 H), 6.81–6.76 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 118.8, 120.0, 120.1, 121.0, 121.2, 123.9, 125.9, 126.1, 126.3, 127.4, 127.6, 128.9, 129.0, 129.2, 129.8, 131.6, 131.8, 132.4, 135.4, 137.4, 137.7, 138.7, 140.1, 141.8, 143.1, 147.7, 164.3, 167.3. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{34}H_{25}N_2O$: 477.1966; found: 477.1970.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-phenylethylidene)-amino)-*N*-(3-bromophenyl)benzamide (3e): Yield: 90%; yellow crystals; R_f (15% EtOAc–Hexane): 0.45. FTIR (KBr): 3649, 3051, 3012, 2971, 2922, 2363, 1942, 1913, 1665, 1589, 1523, 1476, 1446, 1417, 1285, 1249, 1159, 1126, 1064, 994, 956, 913, 877, 768, 726, 697, 674, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.98 (s, 1 H), 8.24–8.21 (m, 1 H), 8.05–8.02 (m, 2 H), 7.57 (d, *J* = 2.0 Hz, 1 H), 7.54 (d, *J* = 4.5 Hz, 1 H), 7.53–7.47 (m, 3 H), 7.42 (d, *J* = 7.2 Hz, 3 H), 7.32–7.28 (m, 1 H), 7.20–7.16 (m, 3 H), 7.15 (d, *J* = 1.9 Hz, 1 H), 7.06 (d, *J* = 7.8 Hz, 2 H), 7.00 (t, *J* = 8.0 Hz, 1 H), 6.90 (s, 1 H), 6.84–6.79 (m, 2 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 118.3, 118.6, 120.0, 120.1, 121.1, 121.2, 122.6, 122.8, 125.8, 125.9, 126.5, 126.7, 127.4, 127.6, 128.8, 129.4, 129.8, 129.9, 130.3, 131.6, 132.1, 132.6, 135.4, 137.4, 137.7, 140.0, 140.1, 141.8, 143.5, 147.6, 164.3, 167.4. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{34}H_{24}BrN_2O$: 557.1072; found: 557.1060.

(*Z*)-2-((2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)-amino)-*N*-(*p*-toluenesulfonyl)benzamide (3f): Yield: 88%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3009, 2919, 1911, 1652, 1593, 1564, 1527, 1446, 1404, 1345, 1314, 1280, 1248, 1177, 1124, 1090, 1019, 881, 849, 812, 767, 729, 696, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.70 (s, 1 H), 8.23 (dd, *J* = 6.0, 3.5 Hz, 1 H), 8.06–8.03 (m, 2 H), 7.57–7.52 (m, 2 H), 7.48 (t, *J* = 7.7 Hz, 2 H), 7.39 (d, *J* = 7.2 Hz, 2 H), 7.31 (dd, *J* = 14.2, 7.8 Hz, 3 H), 7.20–7.14 (m, 4 H), 7.09 (d, *J* = 7.8 Hz, 1 H), 6.97 (d, *J* = 8.3 Hz, 2 H), 6.91 (s, 1 H), 6.81 (ddd, *J* = 11.9, 6.6, 2.4 Hz, 2 H), 2.20 (s, 3 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 20.9, 118.9, 119.9, 120.0, 120.1, 120.9, 121.2, 125.9, 126.1, 126.3, 127.4, 127.6, 128.9, 129.2, 129.5, 129.7, 129.8, 131.5, 131.8, 132.4, 133.4, 135.5, 136.1, 137.4, 137.8, 140.1, 141.8, 143.1, 147.7, 164.1, 167.1. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{35}H_{27}N_2O$: 491.2123; found: 491.2122.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-(*p*-toluenesulfonyl)-ethylidene)amino)-*N*-phenylbenzamide (3g): Yield: 87%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3566, 3057, 2921, 2852, 2364, 1718, 1666, 1597, 1561, 1538, 1495, 1446, 1315, 1280, 1247, 1178, 1121, 1036, 824, 776, 753, 730, 692, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.82 (s, 1 H), 8.22 (dd, *J* = 6.0, 3.5 Hz, 2 H), 7.94 (d, *J* = 8.2 Hz, 2 H), 7.54 (dd, *J* = 11.8, 7.5 Hz, 2 H), 7.48 (dd, *J* = 7.4, 2.4 Hz, 3 H), 7.31–7.27 (m, 1 H), 7.20–7.15 (m, 6 H), 7.14–7.10 (m, 3 H), 6.96 (t, *J* = 7.4 Hz, 1 H), 6.90 (s, 1 H), 6.84–6.76 (m, 2 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 21.8, 119.2, 119.9, 120.0, 120.1, 121.1, 123.9, 125.9, 126.0, 126.1, 127.5, 127.6, 128.9, 129.0, 129.7, 129.8, 130.0, 131.5, 131.9, 134.6, 135.5, 137.7, 138.7, 140.0, 141.7, 142.9, 143.1, 147.8, 164.4, 167.1. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{35}H_{27}N_2O$: 491.2123; found: 491.2123.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-(*p*-toluenesulfonyl)-ethylidene)amino)-*N*-(3-bromophenyl)benzamide (3h): Yield: 91%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3772, 3050, 3009, 2922, 2852, 1938, 1661, 1589, 1553, 1418, 1351, 1313, 1300, 1286, 1251, 1224, 1180, 1158, 1043, 773, 724, 695, 625 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 11.04 (s, 1 H), 8.23–8.20 (m, 1 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 7.57–7.52 (m, 3 H), 7.49–7.47 (m, 2 H), 7.29 (td, *J* = 7.5, 0.9 Hz, 1 H), 7.24–7.19 (m, 3 H), 7.17 (s, 1 H), 7.16–7.13 (m, 2 H), 7.10 (s, 1 H), 7.07 (dd, *J* = 6.5, 1.6 Hz, 1 H), 7.01 (d, *J* = 7.9 Hz, 1 H), 6.89 (s, 1 H), 6.85–6.80 (m, 2 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 21.8, 118.4, 118.8, 120.0, 120.1, 121.1, 121.2, 122.6, 122.8, 125.8, 126.0, 126.3, 126.7, 127.4, 127.6, 128.8, 129.8, 129.9, 130.2, 130.4, 131.4, 131.5, 132.1, 134.8, 135.5, 137.8, 140.1, 141.8, 143.2, 143.4, 143.7, 164.4, 167.2. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{35}H_{26}BrN_2O$: 571.1206; found: 571.1213.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-(*p*-toluenesulfonyl)-ethylidene)amino)-*N*-(*p*-toluenesulfonyl)benzamide (3i): Yield: 88%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3465, 3361, 3271, 3171, 3040, 2917, 2854, 2363, 1920, 1715, 1658, 1539, 1512, 1473, 1446, 1405, 1319, 1281, 1246, 1176, 1128, 1089, 1039, 1014, 983, 938, 895, 851, 815, 777, 728, 693, 664, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.75 (s, 1 H), 8.22 (dd, *J* = 5.9, 3.6 Hz, 1 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 7.54 (dd, *J* = 11.7, 7.5 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.28 (dd, *J* = 10.9, 4.0 Hz, 1 H), 7.18 (d, *J* = 8.7 Hz, 2 H), 7.11 (dd, *J* = 6.1, 3.3 Hz, 3 H), 6.98 (d, *J* = 8.2 Hz, 2 H), 6.90 (s, 1 H), 6.84–6.79 (m, 1 H), 6.77 (dd, *J* = 5.9, 3.2 Hz, 1 H), 2.34 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 21.0, 21.8, 119.3, 119.9, 120.0, 121.0, 121.1, 125.9, 126.0, 127.4, 127.5, 128.9, 129.5, 129.7, 130.0, 131.4, 131.7, 133.4, 135.5, 136.2, 137.7, 140.0, 141.7, 142.8, 143.0, 147.8, 164.2, 170.0. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{36}H_{29}N_2O$: 505.2279; found: 505.2273.

(*Z*)-2-((2-(9*H*-Fluoren-9-ylidene)-1-(*p*-toluenesulfonyl)-ethylidene)amino)-*N*-(3,5-dimethylphenyl)benzamide (3j): Yield: 75%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3163, 3057, 2961, 3919, 2850, 2359, 1910, 1717, 1658, 1594, 1558, 1537, 1502, 1469, 1446, 1405, 1313, 1280, 1252, 1176, 1130, 1092, 1043, 937, 880, 862, 826, 777, 728, 695, 662, 620 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.84 (s, 1 H), 8.32 (dd, *J* = 5.9, 3.6 Hz, 1 H), 8.03 (d, *J* = 8.2 Hz, 1 H), 7.64 (dd, *J* = 11.5, 7.5 Hz, 2 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.42–7.36 (m, 2 H), 7.30–7.26 (m, 4 H), 7.22 (dd, *J* = 6.7, 3.1 Hz, 3 H), 7.18 (s, 1 H), 7.03 (d, *J* = 8.2 Hz, 1 H), 6.98 (s, 1 H), 6.93 (td, *J* = 7.7, 0.9 Hz, 1 H), 6.86 (dd, *J* = 5.9, 3.2 Hz, 1 H), 2.44 (s, 3 H), 2.20 (s, 3 H), 2.15 (s, 3 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 19.3, 19.8, 21.7, 117.4, 119.1, 119.9, 120.0, 120.9, 121.2, 121.3, 125.9, 126.0, 126.1, 127.5, 127.6, 128.9, 129.7, 129.9, 130.0, 131.4, 131.7, 132.1, 134.8, 135.6, 136.5, 1370, 137.8, 140.0, 141.7, 142.9, 142.9, 147.7, 134.1, 166.9. HRMS (ESI): *m*/*z* [M + H] calcd for $C_{37}H_{31}N_2O$: 519.2436; found: 519.2438.

(*Z*)-2-((1-(4-Bromophenyl)-2-(9*H*-fluoren-9-ylidene)-ethylidene) amino)-*N*-phenylbenzamide (3k): Yield: 84%; yellow solid; R_f (10% EtOAc–Hexane): 0.47. FTIR (KBr): 3645, 3052, 3010, 2970, 2932, 2363, 1942, 1913, 1665, 1589, 1523, 1476, 1446, 1417, 1285, 1249, 1159, 1126, 1064, 994, 956, 877, 768, 726, 674, 623 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.55 (s, 1 H), 8.25–8.21 (m, 1 H), 7.93–7.91 (m, 2 H), 7.58–7.53 (m, 4 H), 7.49–7.42 (m, 3 H), 7.33–7.29 (m, 1 H), 7.21 (dd, *J* = 10.8, 4.3 Hz, 4 H), 7.18 (d, *J* = 0.8 Hz, 1 H), 7.17 (dd, *J* = 2.5, 1.0 Hz, 1 H), 7.05 (d, *J* = 7.7 Hz, 1 H), 6.99 (dd, *J* = 10.0, 3.7 Hz, 1 H), 6.88–6.85 (m, 2 H), 6.80–6.78 (m, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 118.2, 120.0, 120.1, 120.2, 120.9, 121.2, 124.1, 125.8, 126.5, 127.3, 127.6, 127.7, 129.2, 130.0, 130.1, 130.2, 131.6, 132.0, 132.6, 135.3, 136.3, 137.6, 138.6, 140.1, 141.9, 143.6, 147.5, 164.2, 166.4. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{34}H_{24}BrN_2O$: 557.1052; found: 557.1053.

(*Z*)-*N*-(3-Bromophenyl)-2-((1-(4-bromophenyl)-2-(9*H*-fluoren-9-ylidene)ethylidene)amino)benzamide (3l): Yield: 83%; yellow solid; R_f (15% EtOAc–Hexane): 0.48. FTIR (KBr): 3060, 2923, 2850, 1668, 1589, 1531, 1478, 1445, 1417, 1304, 1284, 1247, 1171, 1121, 1072, 1007, 859, 835, 774, 727, 680, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.78 (s, 1 H), 8.24–8.21 (m, 1 H), 7.92–7.89 (m, 2 H), 7.56 (t, *J* = 5.5 Hz, 4 H), 7.52 (dd, *J* = 6.9, 5.0 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 1 H), 7.44–7.41 (m, 1 H), 7.30 (dt, *J* = 7.5, 3.7 Hz, 1 H), 7.23–7.20 (m, 1 H), 7.18 (s,

2 H), 7.09 (dd, *J* = 6.6, 1.8 Hz, 1 H), 7.06–7.03 (m, 2 H), 6.87 (dd, *J* = 7.6, 1.0 Hz, 1 H), 6.85 (s, 1 H), 6.82–6.80 (m, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 117.9, 118.2, 120.1, 120.3, 121.0, 121.3, 122.7, 122.8, 125.8, 125.9, 126.7, 126.9, 127.5, 127.9, 127.7, 130.1, 130.2, 130.3, 130.5, 131.6, 132.2, 132.7, 135.2, 136.4, 137.6, 139.8, 140.1, 141.9, 143.9, 147.4, 164.2, 166.5. HRMS (ESI): *m*/*z* [M + 4] calcd for $C_{34}H_{23}Br_2N_2O$: 637.0177; found: 637.1037.

(*Z*)-*N*-(3-Bromophenyl)-2-((2-(2,7-dibromo-9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzamide (3m): Yield: 69%; yellow solid; R_f (15% EtOAc–Hexane): 0.49. FTIR (KBr): 3056, 2919, 2849, 1734, 1671, 1589, 1533, 1476, 1447, 1422, 1307, 1251, 1063, 1003, 952, 879, 810, 773, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 10.97 (s, 1 H), 8.30–8.26 (m, 1 H), 8.00–7.97 (m, 2 H), 7.62 (d, *J* = 1.4 Hz, 1 H), 7.58–7.54 (m, 2 H), 7.49 (d, *J* = 7.8 Hz, 2 H), 7.43 (d, *J* = 1.4 Hz, 1 H), 7.41–7.35 (m, 3 H), 7.31 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.24–7.21 (m, 2 H), 7.14 (d, *J* = 1.4 Hz, 1 H), 7.06 (dd, *J* = 6.8, 1.6 Hz, 1 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 6.98 (s, 1 H), 6.83–6.79 (m, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 118.4, 121.1, 121.2, 121.3, 121.4, 121.5, 121.9, 122.6, 122.9, 124.6, 126.1, 126.8, 127.0, 128.7, 129.2, 129.6, 130.2, 131.9, 132.1, 133.0, 136.7, 137.2, 137.9, 139.3, 139.7, 140.0, 141.3, 147.0, 164.0, 166.1. HRMS (ESI): *m*/*z* [M + 6] calcd for $C_{34}H_{21}Br_3N_2O$: 716.9222; found: 716.9244.

(*E*)-5-Bromo-2-((2-bromo-2(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzamide (4a): Yield: 60%; yellow solid; R_f (15% EtOAc–Hexane): 0.43. FTIR (KBr): 3400, 3059, 1664, 1604, 1576, 1462, 1447, 1408, 1344, 1315, 1263, 1204, 1181, 1096, 1056, 1024, 936, 851, 811, 779, 730, 691, 649, 620 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.52 (d, *J* = 7.9 Hz, 1 H), 8.23 (d, *J* = 2.3 Hz, 1 H), 7.98 (dd, *J* = 5.3, 3.3 Hz, 2 H), 7.87 (s, 1 H), 7.61 (d, *J* = 7.2 Hz, 1 H), 7.56 (d, *J* = 7.5 Hz, 1 H), 7.50–7.46 (m, 1 H), 7.39 (ddd, *J* = 9.6, 7.0, 4.0 Hz, 3 H), 7.31 (d, *J* = 7.9 Hz, 1 H), 7.25 (ddd, *J* = 7.3, 6.8, 3.8 Hz, 2 H), 7.17 (dd, *J* = 6.4, 2.1 Hz, 1 H), 6.98 (td, *J* = 7.8, 1.1 Hz, 1 H), 6.62 (d, *J* = 8.5 Hz, 1 H), 6.05 (s, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 113.1, 119.3, 119.9, 120.0, 120.6, 124.4, 126.4, 126.6, 127.6, 127.9, 128.6, 129.5, 129.6, 130.4, 132.7, 134.1, 134.2, 134.9, 136.2, 136.3, 139.9, 140.3, 141.5, 146.2, 165.6, 166.6. HRMS (ESI): *m*/*z* [M + 4] calcd for $C_{28}H_{19}Br_2N_2O$: 560.9864; found: 560.9847.

(*E*)-2-((2-Bromo-2-(9*H*-fluoren-9-ylidene)-1-(*p*-toluenesulfonyl) ethylidene)amino)benzamide (4b): Yield: 75%; yellow solid; R_f (15% EtOAc–Hexane): 0.45. FTIR (KBr): 3608, 3440, 3341, 3159, 3059, 2919, 2852, 1670, 1563, 1492, 1471, 1445, 1374, 1290, 1267, 1204, 1181, 1113, 1059, 1019, 977, 926, 834, 777, 727, 660, 624 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.51 (d, *J* = 7.9 Hz, 1 H), 8.11–8.07 (m, 1 H), 7.96 (s, 1 H), 7.88 (d, *J* = 8.3 Hz, 2 H), 7.61–7.53 (m, 2 H), 7.39–7.33 (m, 2 H), 7.26–7.18 (m, 4 H), 7.06 (dd, *J* = 5.9, 3.5 Hz, 2 H), 7.01–6.97 (m, 1 H), 6.74–6.71 (m, 1 H), 5.95 (s, 1 H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 21.7, 114.2, 119.0, 119.9, 120.0, 124.7, 125.7, 126.4, 127.6, 128.0, 128.7, 129.5, 130.2, 130.3, 131.4, 131.8, 132.2, 136.5, 136.6, 139.6, 140.3, 141.5, 143.4, 147.5, 164.9, 168.3. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{29}H_{22}BrN_2O$: 495.0995; found: 495.1180.

(*E*)-2-((2-Bromo-2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)benzenesulfonamide (4c): Yield: 73%; yellow solid; R_f (15% EtOAc–Hexane): 0.44. FTIR (KBr): 3358, 3260, 2920, 1915, 1641, 1611, 1530, 1444, 1344, 1276, 1254, 1209, 1171, 1128, 1070, 1024, 942, 857, 832, 807, 772, 689, 620 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.58 (d, *J* = 7.9 Hz, 1 H), 7.98–7.93 (m, 3 H), 7.66 (d, *J* = 7.6 Hz, 1 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.45–7.39 (m, 3 H), 7.38–7.35 (m, 2 H), 7.29–7.24 (m, 2 H), 7.16–7.11 (m, 2 H), 7.00 (td, *J* = 7.9, 1.0 Hz, 1 H), 6.90–6.87 (m, 1 H), 5.39 (s, 2 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 21.0, 21.8, 119.3, 120.0, 121.0, 121.1, 125.9, 126.0, 127.4, 127.5, 128.9, 129.5, 129.7, 129.8, 131.4, 131.7, 133.4, 134.6, 135.5, 136.2, 137.7, 140.0, 141.7, 142.8, 143.0, 147.8, 164.2, 166.9. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{27}H_{20}BrN_2O_2S$: 517.0408; found: 517.0420.

(*E*)-2-((2-Bromo-2-(9*H*-fluoren-9-ylidene)-1-phenylethylidene)amino)-5-iodobenzamide (4d): Yield: 72%; yellow solid; R_f (15% EtOAc–Hexane): 0.43. FTIR (KBr): 3370, 3327, 3145, 3063, 2921, 2774, 2252, 1959, 1903, 1811, 1669, 1596, 1565, 1445, 1404, 1347, 1314, 1260, 1202, 1152, 1087, 1052, 1022, 935, 904, 872, 845, 801, 774, 727, 688, 645, 622 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 8.52 (d, *J* = 7.9 Hz, 1 H), 8.40 (d, *J* = 2.1 Hz, 1 H), 7.99–7.96 (m, 2 H), 7.84 (d, *J* = 2.6 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.56–7.54 (m, 1 H), 7.47–7.44 (m, 1 H), 7.41–7.33 (m, 5 H), 7.30 (d, *J* = 7.9 Hz, 1 H), 7.27–7.19 (m, 2 H), 6.97 (td, *J* = 7.8, 1.1 Hz, 1 H), 6.49–6.46 (m, 1 H). ^{13}C NMR ($CDCl_3$/TMS, 100.6 MHz): δ = 90.1, 113.2, 120.0, 120.1, 120.9, 124.5, 126.5, 126.6, 127.7, 128.0, 128.8, 129.6, 129.7, 130.5, 132.9, 134.2, 136.3, 136.4, 139.9, 140.1, 140.4, 140.9, 141.6, 146.9, 165.6, 166.8. HRMS (ESI): *m*/*z* [M + 2] calcd for $C_{28}H_{19}BrIN_2O$: 606.9705; found: 606.9719.