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Cascade Reactions

Cu/Pd-Catalyzed Cascade Reactions of Cyclic Diaryliodoniums and Alkynes – Access to Fluorenes with Conjugate Enynes/Dienes

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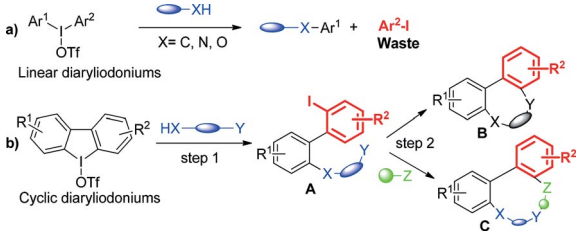
Abstract: Unlike the widely studied linear diaryliodoniums as electrophilic arylating reagents, cyclic diaryliodoniums have the potential to initiate dual arylations with atom and step economy. In our current work, cascade reactions of cyclic diaryliodoniums and two equivalent alkynes have been successfully achieved under mild conditions, catalyzed by CuI/$PdCl_2(PPh_3)_2$. The transformation could also be realized in a stepwise way with two different alkynes or with one alkyne and one alkene. The reaction enables a rapid access to a variety of complex fluorenes containing conjugate enyne and diene fragments.

Introduction

Linear diaryliodoniums are applied widely as electrophilic arylating reagents in both transition-metal-catalyzed and metal-free reactions with various nucleophiles.[1] In the arylation reactions with linear diaryliodoniums, an unavoidable problem is that an unwanted iodoarene is produced along with the desired product and often discarded (Scheme 1).[2] However, this problem can be overcome with cyclic diaryliodoniums because their generated iodoarenes are part of the arylated products **A**.[3] Moreover, a cascade reaction can be set up if the incorporated iodoarenes **A** continue further transformations to generate the more-complex molecules **B** and **C**. However, the application of cyclic diaryliodoniums as organic synthons remains unexplored compared to the application of the well-studied linear diaryliodoniums.[4]

1,1-Diphenylethene is an important molecular scaffold present in clinical drugs or drug candidates. For example, the anticancer drugs Tamoxifen[5] and Bexarotene[6] feature a common 1,1-diphenylethene moiety (Figure 1). Meanwhile, conjugate enynes are important building motifs in biologically active compounds,[7] functional materials,[8] and fine chemicals.[9] To obtain these unique conjugate enyne fragments, few methods



Scheme 1. Arylation with linear and cyclic diaryliodoniums.

are available currently.[10] Similarly, conjugate dienes are valuable products or intermediates in organic chemistry.[11] Although numerous methods are available to prepare di- or trisubstituted dienes, effective methods to prepare more highly substituted dienes are limited.[12]

In our previous study with cyclic diaryliodoniums **1** as synthons, we successfully achieved two types of three-component reaction with terminal alkynes **2** and a third reactant, either an azide or a boronic acid (Scheme 2).[13] These two different reactions were mediated by different catalytic systems and conditions, and the order of the cascade reaction was interestingly decided by a third reactant. The multicomponent reaction with sodium azide was mediated by CuI. During this transformation, the azidation of the cyclic diaryliodoniums occurred before copper(I)-catalyzed alkyne–azide cycloaddition (CuAAC) and Ullmann reactions to afford triazolophenanthridines **3**. However, in the reactions with boronic acids, a dual transition-metal Pd and Cu catalysis system had to be applied. The reaction began with the alkynylation of the cyclic iodoniums, followed by an intramolecular insertion to the triple bond and a Suzuki reaction to generate fluorenes **4**. Herein, we demonstrate another multicomponent cascade reaction with cyclic diaryliodoniums and two molecular alkynes under mild conditions to provide fluorenes **5**, the structures of which feature the combination of 1,1-diphenylethene and conjugate enyne fragments.

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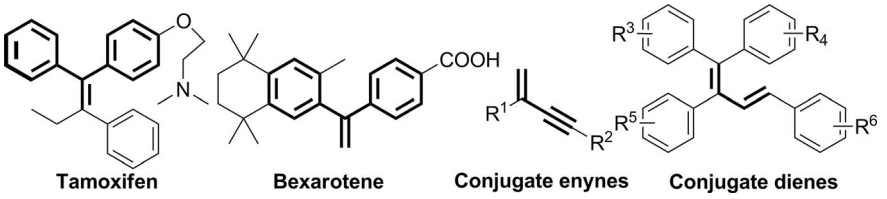
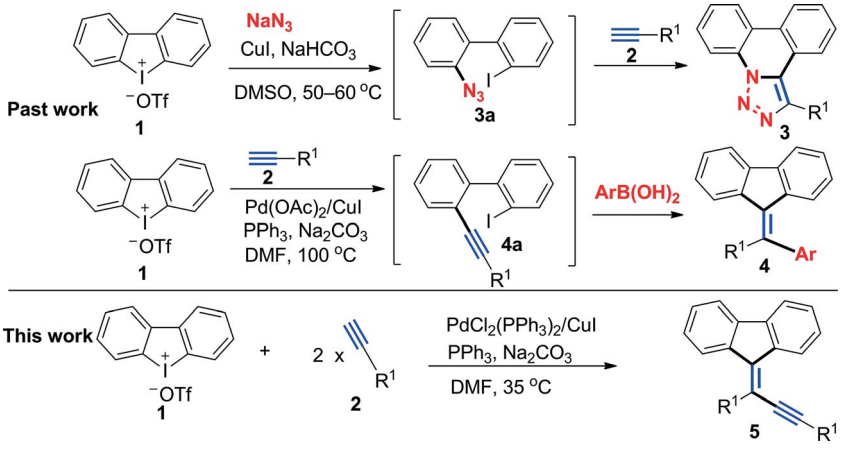


Figure 1. Representative compounds containing conjugate enynes and dienes.[5–9]



Scheme 2. Diversified multicomponent reactions with cyclic diaryliodoniums and alkynes.

These one-pot transformations were also realized by two-step reactions.

Results and Discussion

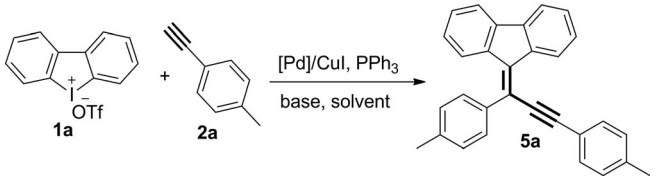
In our previous work, intermediate **4a** was conveniently prepared from the cyclic diaryliodonium **1a** and *p*-tolylacetylene (**2a**) in the presence of CuI/$Pd(OAc)_2$ at ambient temperature (Scheme 2).[13a] However, unexpectedly, a new compound, **5a**, was obtained with a trace of **4a** when the reaction was run at ambient temperature in a different season. The structure of **5a** was then determined by NMR and mass spectroscopy to be a fluorene, as was verified by a later X-ray diffraction study of another compound (**6f**). On one hand, fluorene-based derivatives are present in biologically active compounds and advanced materials.[14] On the other hand, fluorene **5a** might be endowed with the biological and chemical properties from the 1,1-diphenylethene and conjugate enyne moieties. Thus, it was of our interest to investigate this finding.

After a careful examination of the reaction conditions, we finally realized that the two ambient temperatures were different, that is, 35 °C in the current report and 20 °C in the previous study; this implies that the temperature can guide the direction of the reactions between cyclic iodoniums and terminal alkynes. At a slightly higher temperature, **4a** was further transformed into **5a**, a unique fluorene with a conjugate enyne fragment. To the best of our knowledge, there are very few synthetic reports on such fluorenes.[15,16] Moreover, the reported methods have some limitations. For example, the 2,2′-diiodobiphenyl substrates are limited and not easy to prepare[15] or the reactions have to be performed at subzero temperatures with sensitive organolithiums.[16] Thus, our initial discovery might serve as a concise method to access a variety of fluorenes containing conjugate enynes.

At the beginning of our investigation, a series of palladium catalysts, bases, and solvents were screened to optimize the reaction conditions (Table 1). Compound **5a** was obtained in a good yield when iodonium **1a** reacted with 2.5 equiv. of *p*-tolylacetylene **2a** in the presence of catalytic $Pd(OAc)_2$/CuI in *N*,*N*-dimethylformamide (DMF; Table 1, Entry 1). Other palladium catalysts available in our laboratory were also tried, and $PdCl_2(PPh_3)_2$ gave the best yield (Table 1, Entries 2–6). Most of the screened bases gave good-to-excellent yields, except KO*t*Bu (Table 1, Entries 7–12). A base was critical to the reaction, and no product was observed in its absence (Table 1, Entry 13). In the screening of other common solvents, dimethyl sulfoxide (DMSO) also gave a good yield, whereas dichloromethane, 2-propanol, and toluene led to poor yields (Table 1, Entries 14–17). Our further studies showed that the best yield was obtained at 35 °C, and higher or lower temperatures decreased the conversion (Table 1, Entries 18 and 19).

With the optimal reaction condition in hand, the scope of alkyne **2** was then investigated (Figure 2). Regardless of their electronic properties, all of the arylalkynes provided the desired products in moderate-to-good yields (**5b**–**5k**). It seemed that arylalkynes with electron-withdrawing groups provided higher yields than those with electron-donating groups (**5g**–**5k** vs. **5b**–**5f**). Notably, an arylalkyne with an amine group was tolerable in this transformation (**5f**), although amines reacted with cyclic diaryliodoniums in our previous study.[3a] To our delight, a volatile alkylalkyne, propargyl acetate, was compatible with the reaction conditions and provided the desired product (**5l**).

Table 1. Reaction condition optimization.[a]



Entry	Catalyst	Base	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	Na_2CO_3	DMF	75
2	$PdCl_2$	Na_2CO_3	DMF	82
3	$PdCl_2(CH_3CN)_2$	Na_2CO_3	DMF	75
4	$Pd(dba)_2$	Na_2CO_3	DMF	75
5	$PdCl_2$(dppf)	Na_2CO_3	DMF	77
6	$PdCl_2(PPh_3)_2$	Na_2CO_3	DMF	94
7	$PdCl_2(PPh_3)_2$	K_2CO_3	DMF	87
8	$PdCl_2(PPh_3)_2$	Cs_2CO_3	DMF	83
9	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	75
10	$PdCl_2(PPh_3)_2$	KO*t*Bu	DMF	22
11	$PdCl_2(PPh_3)_2$	NaOAc	DMF	86
12	$PdCl_2(PPh_3)_2$	Et_3N	DMF	69
13	$PdCl_2(PPh_3)_2$	–	DMF	ND
14	$PdCl_2(PPh_3)_2$	Na_2CO_3	DMSO	74
15	$PdCl_2(PPh_3)_2$	Na_2CO_3	*i*PrOH	17
16	$PdCl_2(PPh_3)_2$	Na_2CO_3	toluene	36
17	$PdCl_2(PPh_3)_2$	Na_2CO_3	DCE	13
18[c]	$PdCl_2(PPh_3)_2$	Na_2CO_3	DMF	60
19[d]	$PdCl_2(PPh_3)_2$	Na_2CO_3	DMF	15

[a] Reaction conditions: **1a** (70.1 μmol), **2a** (2.5 equiv.), CuI (10 mol-%), Pd catalyst (10 mol-%), PPh_3 (30 mol-%), base (4.0 equiv.), 35 °C, 15 h, Ar. Note: ND = not detected; DCE = 1,2-dichloroethane, dba = dibenzylideneacetone, dppf = (diphenylphosphino)ferrocene. [b] HPLC yield. [c] 70 °C. [d] 20 °C.

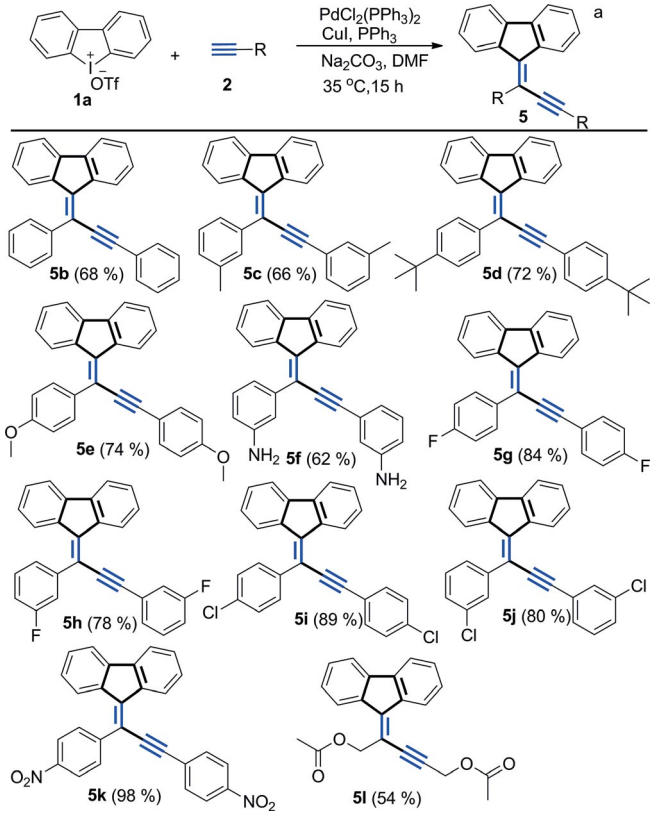


Figure 2. The scope of alkynes **2**. [a] Isolated yield.

The scope of the cyclic diaryliodonium **1** was also investigated (Figure 3). Symmetrical diaryliodoniums with electron-donating groups and those with electron-withdrawing groups both provided good yields (**6a**–**6d**). Then, unsymmetrical iodoniums were also studied. It has been reported that a methyl group *ortho* to the I^{III} center accelerates the elimination rate, and this has been called the "*ortho* effect".[17] However, the groups of Gaunt and Sanford have observed that large substituents in unsymmetrical linear diaryliodoniums led to regioselective arylation at the less-hindered aryl side.[18,19] Our previous study also demonstrated that steric effects dominated over *ortho* effects in the arylation of azides with unsymmetrical cyclic diaryliodoniums.[13b] Accordingly, a series of unsymmetrical diaryliodoniums were synthesized with a 2,4-dimethyl substitution pattern on one aryl ring. Subsequently, these unsymmetrical iodoniums were subject to the standard reaction conditions. To our delight, high regioselectivity was obtained for these desired products in modest-to-good yields regardless of the electronic properties of the aryl ring on the other side (**6f**–**6i**). The structure of **6f**, as determined by X-ray diffraction (Figure 4), implies that *ortho* effects are dominant over steric effects to decide the regioselectivity.

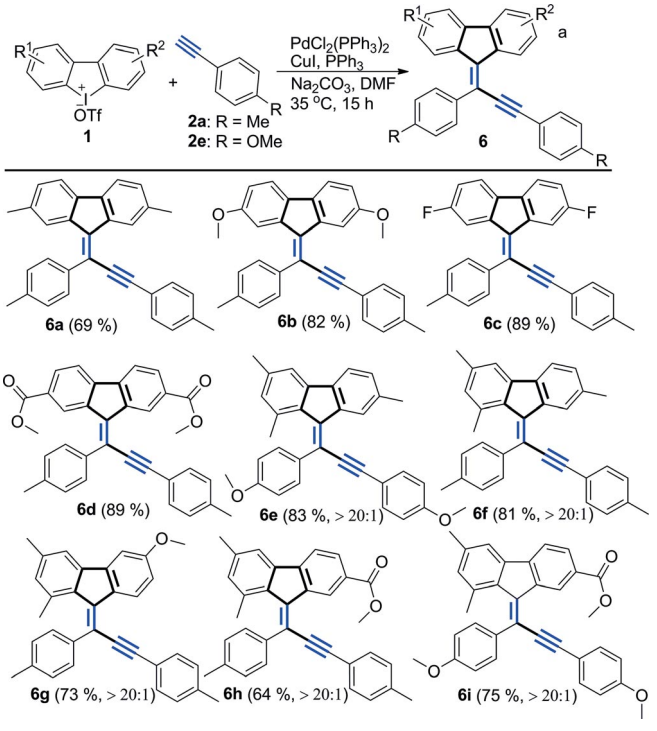


Figure 3. The scope of cyclic diaryliodoniums **1**. [a] Isolated yield.

It is worth mentioning that the two molecular alkynes involved in the aforementioned reactions are identical (Figures 2 and 3). However, it was our hypothesis that more structurally diverse compounds could be obtained if such transformations were performed stepwise. Thus, intermediate **7** was prepared in a large scale at a lower temperature, that is, 20 °C. Then, a series of different alkynes **2** were employed to react with **7** (Figure 5). The reactions of **7** with the alkynes in the next step provided the desired products in good yields and further broadened the structural complexity of the fluorenes (**8a**–**8i**).

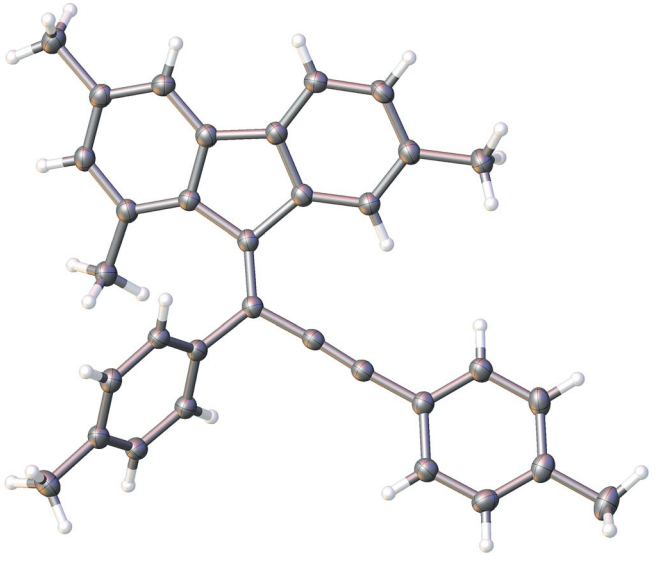


Figure 4. The crystal structure of **6f**.

Meanwhile, alkenes including acrylate ester, styrene, and 4-vinylpyridine moieties were also able to couple with **7** smoothly to generate fluorenes with conjugate dienes in good yields (**9a**–**9c**). The one-pot operation of these two-step transformations would be valuable; however, this currently has not provided promising results. The optimization of the one-pot transformation is underway.

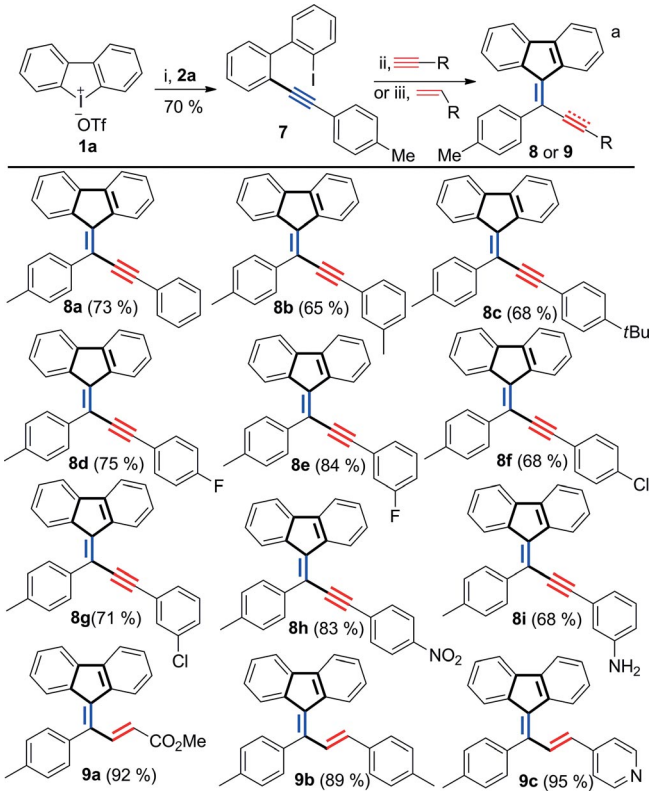
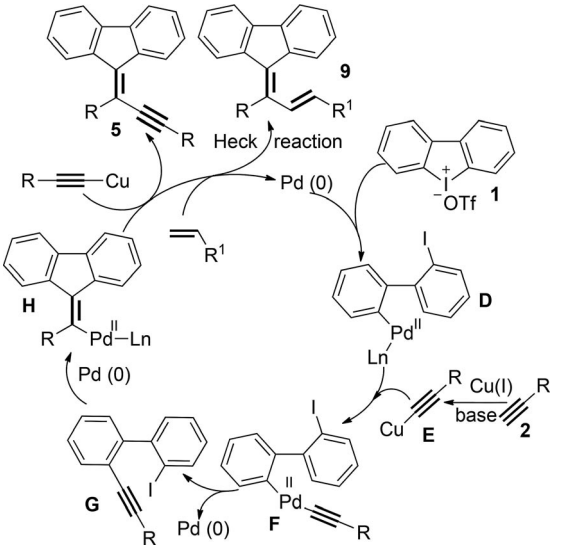


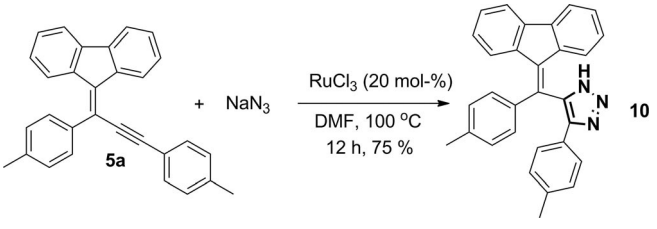
Figure 5. Stepwise transformations. Conditions: (i) **2a** (1.2 equiv.), $PdCl_2(PPh_3)_2$ (0.1 equiv.), CuI (0.1 equiv.), PPh_3 (0.3 equiv.), Na_2CO_3 (3 equiv.), DMF, 20 °C, 12 h; (ii) same as (i) except alkyne (2.0 equiv.), 35 °C, 15 h; (iii) alkene (2.0 equiv.), $Pd(OAc)_2$ (0.1 equiv.), PPh_3 (0.3 equiv.), Na_2CO_3 (3 equiv.), DMF, 110 °C, 15 h. [a] Isolated yield.

On the basis of our previous experiments and the current observations, a potential reaction mechanism is proposed (Scheme 3). Firstly, Pd^0 formed in situ from Pd^{II} is subjected to oxidative addition with iodonium **1** to generate the palladium(II) species **D**. The transmetallation of **D** with the acetylene copper species **E** from alkyne **2** and the subsequent reductive elimination of intermediate **F** provides an alkynylated intermediate **G**. Then, **G** undergoes another oxidative addition and subsequent intramolecular insertion of a triple bond to form the palladium(II) species **H**. The transmetallation of **H** with an acetylene copper species and final reductive elimination generates product **5**. In the stepwise transformation, a Heck reaction coupling of **H** with an alkene affords **9**.



Scheme 3. The proposed mechanism.

Notably, the obtained fluorenes contain conjugate enyne or diene fragments, which could invite further transformation to make other complex chemical entities. Thus, **5a** was selected to react with sodium azide to install a triazole ring. Indeed, the reaction proceeded smoothly with $RuCl_3$ as a catalyst to provide **10** with multiple fused aromatic rings (Scheme 4). Further investigations to build six-membered rings from **5a** and **10** are underway.



Scheme 4. Further transformation of **5a** to **10**.

Conclusions

We have achieved a cascade reaction with cyclic diaryliodoniums and two molecular alkynes catalyzed by $CuI/PdCl_2(PPh_3)_2$

under mild conditions. A series of functionalized fluorenes featuring conjugate enyne motifs were obtained with our method. In addition, the regioselectivity was resolved for unsymmetrical cyclic diaryliodoniums by installing two methyl groups *ortho* and *para* to the I^{III} center. The transformations could proceed in two steps to further broaden the structural diversity of the fluorenes with a conjugate enyne or diene. The biological evaluations and further structural transformations of these unique fluorenes are underway.

Experimental Section

General Information: All reactions were performed under an argon atmosphere with dried glassware. The cyclic diaryliodoniums were synthesized according to our previously reported procedure.[13] Unless otherwise stated, all reagents obtained from commercial suppliers were used without further purification. The yields for the optimization of conditions were determined by HPLC, and the others are isolated yields. Reaction progress was monitored by thin layer chromatography (TLC) with glass plates coated with silica gel with a fluorescent indicator (GF254), which was visualized with UV light and phosphomolybdic acid. Column chromatography was generally performed with silica gel (200–300 mesh). The ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrometer at 400 and 100 MHz, respectively. The chemical shifts are given in ppm and were referenced to $CDCl_3$ at δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C or to [D_6]DMSO at δ = 2.50 ppm for ^1H and δ = 39.5 ppm for ^{13}C. For multiplets, the signals are reported as intervals. The multiplicity is abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants are expressed in Hertz. The isomer ratios of the final compounds were determined with an Agilent 1260 HPLC system with an Eclipse XDB-C18 column.

General Procedure for the Synthesis of 5 (Exemplified by 5a): To cyclic diaryliodonium **1a** (200 mg, 467.1 μmol) were added Na_2CO_3 (198.0 mg, 1.87 mmol), CuI (17.8 mg, 93.4 μmol), $Pd(PPh_3)_2Cl_2$ (32.8 mg, 46.7 μmol), and PPh_3 (36.8 mg, 140.1 μmol). The reaction vessel was evacuated and backfilled with argon three times, and a solution of *p*-tolylacetylene (**2a**; 175.0 μL, 1.4 mmol) in DMF (8.0 mL) was added with a syringe. The reaction mixture was stirred under an Ar atmosphere and heated to 35 °C with an oil bath for 15 h. The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (10 mL × 2) and brine (10 mL) successively, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography [EtOAc/petroleum ether (EtOAc/PE) = 1:500] to give 9-(1,3-di-*p*-tolylprop-2-yn-1-ylidene)-9-*H*-fluorene (**5a**) as a yellow solid (167.1 mg, 94 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.95–8.92 (m, 1 H), 7.77–7.75 (m, 1 H), 7.70–7.68 (m, 1 H), 7.51–7.49 (m, 4 H), 7.45–7.39 (s, 2 H), 7.35–7.32 (m, 2 H), 7.27–7.25 (m, 1 H), 7.23–7.20 (m, 2 H), 6.96–6.92 (m, 1 H), 6.66–6.64 (m, 1 H), 2.51 (s, 3 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 139.8, 139.3, 138.5, 138.4, 137.9, 137.2, 131.7, 129.8, 129.4, 129.1, 128.8, 128.3, 127.4, 126.7, 125.6, 125.0, 123.5, 120.4, 119.5, 102.5, 91.9, 21.7, 21.6 ppm. ESI-HRMS: calcd. for $C_{30}H_{23}$ $[M + H]^+$ 383.1794; found 383.1770.

9-(1,3-Diphenylprop-2-yn-1-ylidene)-9*H*-fluorene (5b): By the general procedure for **5a**, **5b** was obtained as yellow solid (112.6 mg, 68 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.89 (d, *J* = 7.2 Hz, 1 H), 7.73 (d, *J* = 6.8 Hz, 1 H), 7.66 (d, *J* = 7.6 Hz, 1 H), 7.58–7.57 (m, 4 H), 7.54–7.48 (m, 3 H), 7.42–7.39 (m, 5 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 6.89 (t, *J* = 7.6 Hz, 1 H), 6.48 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 140.5, 140.4, 140.1, 138.3, 137.7, 131.8, 129.2, 129.1, 129.0, 128.7, 128.6, 127.5, 126.8, 125.7, 125.1, 123.4, 123.1, 119.6, 119.5, 102.4, 92.1 ppm. ESI-HRMS; calcd. for $C_{28}H_{19}$ $[M + H]^+$ 355.1481; found 355.1476.

9-(1,3-Di-*m*-tolylprop-2-yn-1-ylidene)-9*H*-fluorene (5c): By the general procedure for **5a**, **5c** was obtained as a yellow liquid (117.9 mg, 66 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.21–9.20 (m, 1 H), 7.99–7.97 (m, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.68–7.65 (m, 6 H), 7.56–7.53 (m, 2 H), 7.52–7.59 (m, 1 H), 7.48–7.46 (m, 1 H), 7.44–7.43 (m, 1 H), 7.19–7.15 (m, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H) 2.70 (s, 3 H), 2.62 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 140.4, 140.2, 140.0, 138.8, 138.4, 138.3, 137.8, 132.3, 129.9, 129.6, 129.2, 129.0, 128.9, 128.9, 128.5, 128.4, 127.5, 126.7, 126.1, 125.7, 125.0, 123.4, 123.2, 119.5, 119.5, 102.6, 91.9, 21.6, 21.4 ppm. ESI-HRMS: calcd. for $C_{30}H_{23}$ $[M + H]^+$ 383.1794; found 383.1790.

9-{1,3-Bis[4-(*tert*-butyl)phenyl]prop-2-yn-1-ylidene}-9*H*-fluorene (5d): By the general procedure for **5a**, **5d** was obtained as yellow solid (156.9 mg, 72 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.97–8.95 (m, 1 H), 7.78–7.76 (m, 1 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.58 (s, 1 H), 7.56–7.55 (m, 5 H), 7.46–7.42 (m, 4 H), 7.27–7.23 (m, 1 H), 6.95–6.91 (m, 1 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 1.47 (s, 9 H), 1.39 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 151.7, 140.4, 140.4, 140.0, 138.5, 137.9, 137.1, 131.61, 128.9, 128.7, 128.3, 127.4, 126.9, 126.0, 125.6, 125.6, 125.1, 123.6, 120.5, 119.5, 119.4, 102.5, 91.9, 35.0, 34.9, 31.6, 31.3 ppm. ESI-HRMS: calcd. for $C_{36}H_{35}$ $[M + H]^+$ 467.2733; found 467.2731.

9-[1,3-Bis(4-methoxyphenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5e): By the general procedure for **5a**, **5e** was obtained as a yellow solid (143.3 mg, 74 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.91 (m, 1 H), 7.76 (m, 1 H), 7.68 (d, *J* = 6.8 Hz, 1 H), 7.53–7.52 (m, 4 H), 7.41 (m, 2 H), 7.24 (m, 1 H), 7.05–7.03 (m, 2 H), 6.94–6.92 (m, 3 H), 6.70 (d, 1 H), 3.92 (s, 3 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 159.9, 140.3, 139.4, 138.5, 137.9, 134.2, 133.4, 132.5, 130.6, 128.6, 128.2, 127.4, 126.7, 125.5, 124.9, 123.4, 119.5, 115.6, 114.5, 114.4, 114.3, 102.5, 91.6, 55.5 ppm. ESI-HRMS: calcd. for $C_{30}H_{23}O_2$ $[M + H]^+$ 415.1693; found 415.1683.

3,3′-[3-(9*H*-Fluoren-9-ylidene)prop-1-yne-1,3-diyl]dianiline (5f): By the general procedure for **5a**, **5f** was obtained as a yellow solid (111.3 mg, 62 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.75–8.73 (m, 1 H), 7.74–7.64 (m, 3 H), 7.7–7.53 (m, 1 H), 7.49–7.44 (m, 1 H), 7.41–7.35 (m, 1 H), 7.22 (t, *J* = 7.2 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 7.10 (t, *J* = 7.6 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 6.95–6.91 (m, 1 H), 6.86 (s, 1 H), 6.81–6.77 (m, 1 H), 671–6.65 (m, 1 H), 3.71 (s, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1, 146.5, 140.9, 140.2, 140.2, 139.8, 138.2, 137.6, 130.0, 129.5, 128.8, 128.3, 127.4, 126.8, 125.8, 124.9, 123.8, 123.3, 122.0, 119.4, 118.9, 117.7, 115.9, 115.2, 115.1, 102.6, 91.4 ppm. ESI-HRMS: calcd. for $C_{28}H_{21}N_2$ $[M + H]^+$ 385.1699; found 385.1695.

9-[1,3-Bis(4-fluorophenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5g): By the general procedure for **5a**, **5g** was obtained as a yellow solid (153.2 mg, 84 % yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87–8.85 (m, 1 H), 7.77–7.75 (m, 1 H), 7.70 (d, *J* = 4.2 Hz, 1 H), 7.610–7.55 (m, 4 H), 7.45–7.40 (m, 2 H), 7.30–7.21 (m, 3 H), 77.13 (d, *J* = 8.8 Hz, 2 H), 6.99–6.95 (m, 1 H), 6.56 (d, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 164.2, 161.8, 140.8, 140.6, 140.5, 138.2, 137.5, 135.9, 133.8, 133.7, 131.1, 131.0, 129.2, 128.8, 127.5, 126.9, 125.5, 124.9, 121.6, 119.7, 119.6, 119.4, 116.4, 116.2, 116.2, 116.0, 101.2, 91.7 ppm. ESI-HRMS: calcd. for $C_{28}H_{17}F_2$ $[M + H]^+$ 391.1293; found 391.1289.

9-[1,3-Bis(3-fluorophenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5h): By the general procedure for **5a**, **5h** was obtained as a yellow

solid (142.2 mg, 78 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (d, J = 7.6 Hz, 1 H), 7.63 (d, J = 7.2 Hz, 1 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.42–7.38 (m, 1 H), 7.36–7.30 (m, 2 H), 7.28–7.24 (m, 3 H), 7.21–7.14 (m, 3 H), 7.13–7.08 (m, 1 H), 7.03–6.98 (m, 1 H), 6.83 (t, J = 7.6 Hz, 1 H), 6.41 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5, 163.9, 162.1, 161.4, 141.8, 141.7, 141.5, 140.8, 140.7, 138.0, 137.3, 130.9, 130.8, 130.4, 130.3, 129.5, 129.1, 127.7, 127.6, 127.0, 125.7, 125.0, 125.0, 125.0, 120.6, 119.7, 119.7, 118.6, 118.4, 116.6, 116.4, 116.1, 115.8, 115.6, 100.8, 92.2 ppm. ESI-HRMS: calcd. for $C_{28}H_{17}F_2$ $[M + H]^+$ 391.1293; found 391.1290.

9-[1,3-Bis(3-fluorophenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5i): By the general procedure for **5a**, **5i** was obtained as a yellow solid (176.0 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (m, 1 H), 7.73 (m, 1 H), 7.66 (d, J = 7.2 Hz, 1 H), 7.58–7.56 (m, 4 H), 7.51–7.50 (m, 2 H), 7.42–7.40 (m, 2 H), 7.38–7.37 (m, 2 H), 7.23–7.22 (m, 1 H), 7.15–7.05 (m, 1 H), 6.81 (d, J = 8.4 Hz, 1 H), 6.45 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.1, 140.7, 140.6, 138.3, 138.1, 137.4, 135.3, 134.7, 132.9, 130.7, 129.5, 129.3, 129.1, 128.9, 127.6, 126.9, 125.7, 124.9, 121.6, 121.0, 119.7, 119.7, 101.1, 92.6 ppm. ESI-HRMS: calcd. for $C_{28}H_{17}Cl_2$ $[M + H]^+$ 423.0702; found 423.0705.

9-[1,3-Bis(3-chlorophenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5j): By the general procedure for **5a**, **5j** was obtained as yellow solid (158.2 mg, 80 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 8.0 Hz, 1 H), 7.74 (d, J = 7.2 Hz, 1 H), 7.67 (d, J = 7.2 Hz, 1 H), 7.60 (d, J = 12.4 Hz, 2 H), 7.51–7.26 (m, 9 H), 6.97 (t, J = 8.0 Hz, 1 H), 6.55 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6, 141.4, 140.8, 140.7, 137.9, 137.2, 135.0, 134.6, 131.5, 130.5, 129.9, 129.5, 129.3, 129.2, 129.1, 128.8, 127.7, 127.4, 127.0, 125.7, 125.0, 124.8, 120.4, 119.8, 119.7, 100.7, 92.4 ppm. ESI-HRMS: calcd. for $C_{28}H_{17}Cl_2$ $[M + H]^+$ 423.0702; found 423.0708.

9-[1,3-Bis(4-nitrophenyl)prop-2-yn-1-ylidene]-9*H*-fluorene (5k): By the general procedure for **5a**, **5k** was obtained as a yellow solid (203.4 mg, 98 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 8.0 Hz, 1 H), 8.39 (d, J = 8.4 Hz, 2 H), 8.25 (d, J = 8.0 Hz, 2 H), 7.76 (d, J = 8.0 Hz, 2 H), 7.72 (d, J = 7.6 Hz, 1 H), 7.69–7.65 (m, 3 H), 7.54 (t, J = 8.4 Hz, 1 H), 7.46 (t, J = 7.2 Hz, 1 H), 7.39 (t, J = 7.2 Hz, 1 H), 7.32–7.26 (m, 2 H), 6.91 (t, J = 8.0 Hz, 1 H), 6.43 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.1, 147.7, 145.9, 141.2, 137.6, 136.7, 134.5, 133.5, 132.4, 130.5, 130.3, 129.9, 129.4, 128.6, 127.9, 127.3, 125.6, 125.1, 124.7, 124.0, 120.1, 118.5, 100.1, 95.3 ppm. ESI-HRMS: calcd. for $C_{28}H_{17}N_2O_4$ $[M + H]^+$ 445.1188; found 445.1185.

4-(9*H*-Fluoren-9-ylidene)pent-2-yne-1,5-diyldiacetate (5l): By the general procedure for **5a**, **5l** was obtained as a yellow liquid (87.3 mg, 54 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 7.6 Hz, 1 H), 7.69–7.65 (m, 2 H), 7.57 (d, J = 8.0 Hz, 1 H), 7.37 (t, J = 7.2 Hz, 2 H), 7.30 (t, J = 18.4 Hz, 2 H), 5.31 (s, 2 H), 5.07 (s, 2 H), 2.20–2.16 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 170.3, 143.7, 141.0, 140.5, 137.6, 136.7, 129.5, 129.5, 127.7, 127.6, 126.2, 125.2, 120.0, 119.5, 115.9, 95.4, 86.6, 64.4, 53.0, 21.0, 20.9 ppm. ESI-HRMS: calcd. for $C_{22}H_{19}O_4$ $[M + H]^+$ 347.1278; found 347.1281.

9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-2,7-dimethyl-9*H*-fluorene (6a): By the general procedure for **5a**, **6a** was obtained as a yellow solid (124.5 mg, 69 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 7.40 (d, J = 7.6 Hz, 1 H), 7.35–7.32 (m, 5 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.0 Hz, 3 H), 6.86 (d, J = 7.6 Hz, 1 H), 6.21 (s, 1 H), 2.35 (s, 6 H), 2.24 (s, 3 H), 1.95 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 139.1, 138.7, 138.2, 138.1, 138.1, 137.3, 136.5, 135.7, 131.5, 129.6, 129.4, 129.1, 126.5, 125.8, 122.8, 120.6, 118.9, 102.0, 92.2, 22.2, 21.8, 21.7, 21.5 ppm. ESI-HRMS: calcd. for $C_{32}H_{27}$ $[M + H]^+$ 411.2113; found 411.2109.

9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-2,7-dimethoxy-9*H*-fluorene (6b): By the general procedure for **5a**, **6b** was obtained as a yellow solid (148.7 mg, 82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (d, J = 2.4 Hz, 1 H), 7.51–7.49 (m, 5 H), 7.42 (d, J = 8.0 Hz, 1 H), 7.37–7.35 (m, 2 H), 7.21–7.19 (m, 2 H), 6.77 (dd, J = 2.4, J = 6.0 Hz, 1 H), 6.94 (dd, J = 2.4, J = 6.0 Hz, 1 H), 6.09 (d, J = 2.4 Hz, 1 H), 3.87 (s, 3 H), 3.47 (s, 3 H), 2.48 (s, 3 H), 2.41 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 157.9, 140.1, 139.6, 139.3, 139.1, 138.3, 137.1, 133.9, 133.8, 131.6, 129.8, 129.4, 129.0, 123.3, 120.2, 119.2, 115.2, 115.1, 110.8, 110.6, 102.9, 91.5, 55.7, 54.9, 29.8, 21.7, 21.4 ppm. ESI-HRMS: calcd. for $C_{32}H_{27}O_2$ $[M + H]^+$ 443.2006; found 443.2009.

9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-2,7-difluoro-9*H*-fluorene (6c): By the general procedure for **5a**, **6c** was obtained as a yellow solid (160.5 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (t, J = 12.8 Hz, 1 H), 7.58–7.47 (m, 6 H), 7.40–7.37 (m, 2 H), 7.27–7.24 (m, 2 H), 7.15–7.11 (m, 1 H), 6.98–6.92 (m, 1 H), 6.36–6.30 (m, 1 H), 2.54 (m, 3 H), 2.44 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 163.0, 162.9, 161.3, 160.5, 140.2, 140.1, 139.8, 139.5, 139.4, 139.0, 138.0, 136.2, 135.6, 135.5, 131.7, 131.4, 130.0, 129.5, 129.1, 128.8, 128.7, 126.0, 119.9, 119.8, 115.6, 115.4, 115.1, 112.8, 112.5, 112.4, 112.1, 104.3, 91.3, 21.7, 21.5 ppm. ESI-HRMS: calcd. for $C_{30}H_{21}F_2$ $[M + H]^+$ 419.1606; found 419.1609.

Dimethyl 9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-9*H*-fluorene-2,7-dicarboxylate (6d): By the general procedure for **5a**, **6d** was obtained as a yellow solid (162.2 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.73 (s, 1 H), 8.16 (d, J = 7.6 Hz, 1 H), 7.95 (d, J = 7.6 Hz, 1 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.76 (d, J = 8.4 Hz, 1 H), 7.64 (d, J = 7.6 Hz, 2 H), 7.50–7.42 (m, 2 H), 7.42–7.34 (m, 2 H), 7.25–7.20 (m, 3 H), 3.96 (s, 3 H), 3.78 (s, 3 H), 2.53 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 166.9, 142.8, 142.8, 139.8, 139.1, 138.9, 138.6, 137.8, 136.5, 132.1, 130.4, 129.9, 129.8, 129.7, 129.4, 129.1, 128.9, 127.1, 126.4, 126.2, 120.0, 105.0, 91.4, 52.2, 52.1, 21.8, 21.6 ppm. ESI-HRMS: calcd. for $C_{34}H_{27}O_4$ $[M + H]^+$ 499.1904; found 499.1898.

(*E*)-9-[1,3-Bis(4-methoxyphenyl)prop-2-yn-1-ylidene]-1,3,7-trimethyl-9*H*-fluorene (6e): By the general procedure for **5a**, **6e** was obtained as a yellow solid (161.2 mg, 83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 7.60–7.56 (m, 3 H), 7.41 (d, J = 8.8 Hz, 1 H), 7.34 (s, 1 H), 7.17 (d, J = 7.6 Hz, 1 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 6.63 (s, 1 H), 3.86 (s, 3 H), 3.84 (s, 3 H), 2.46 (s, 3 H), 2.37 (s, 3 H), 1.45 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 159.3, 141.6, 141.2, 138.3, 137.2, 136.4, 135.3, 135.1, 133.1, 133.0, 131.8, 130.9, 128.8, 124.8, 121.9, 119.0, 117.6, 115.8, 114.4, 114.2, 114.1, 114.0, 101.0, 92.5, 55.4, 22.3, 21.9, 21.5 ppm. ESI-HRMS: calcd. for $C_{33}H_{29}O_2$ $[M + H]^+$ 457.2162; found 457.2159.

(*E*)-9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-1,3,7-trimethyl-9*H*-fluorene (6f): By the general procedure for **5a**, **6f** was obtained as a yellow solid (146.3 mg, 81 % yield). The structure of **6f** was determined by X-ray crystal diffraction. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1 H), 7.64 (d, J = 7.6 Hz, 1 H), 7.58 (d, J = 8.0 Hz, 2 H), 7.47 (s, 1 H), 7.45 (s, 1 H), 7.40–7.39 (m, 2 H), 7.28–7.27 (m, 1 H), 7.25 (s, 1 H), 7.23 (s, 2 H), 7.21 (s, 1 H), 6.69 (s, 1 H), 2.53 (s, 3 H), 2.45 (s, 3 H), 2.44 (s, 3 H), 2.43 (s, 3 H), 1.48 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 141.6, 141.4, 139.9, 139.0, 138.5, 137.7, 137.3, 136.4, 135.3, 135.2, 131.5, 131.0, 130.4, 129.5, 129.3, 129.0, 125.0, 122.1, 120.7, 119.0, 117.6, 101.0, 93.0, 22.2, 21.9, 21.7, 21.5, 21.4 ppm. ESI-HRMS: calcd. for $C_{33}H_{29}$ $[M + H]^+$ 425.2269; found 425.2273.

(*E*)-9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-6-methoxy-1,3-dimethyl-9*H*-fluorene (6g): By the general procedure for **5a**, **6g** was obtained as a yellow solid (132.3 mg, 73 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 8.4 Hz, 1 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.28

(d, *J* = 8.4 Hz, 2 H), 7.25 (s, 1 H), 7.15–7.13 (m, 1 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.75 (dd, *J* = 2.4, *J* = 6.0 Hz, 1 H), 6.57 (s, 1 H), 3.82 (s, 3 H), 2.30 (s, 3 H), 2.28 (s, 3 H), 1.32 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 141.8, 141.5, 140.9, 140.0, 139.0, 138.4, 137.6, 136.0, 135.4, 134.4, 131.7, 130.5, 129.4, 129.3, 125.2, 120.7, 120.4, 117.9, 112.6, 104.7, 100.3, 92.9, 55.7, 21.9, 21.7, 21.5, 21.4 ppm. ESI-HRMS: calcd. for $C_{33}H_{29}O$ $[M + H]^+$ 441.2213; found 441.2209.

(*E*)-Methyl 9-(1,3-Di-*p*-tolylprop-2-yn-1-ylidene)-6,8-dimethyl-9*H*-fluorene-2-carboxylate (6h): By the general procedure for **5a**, **6h** was obtained as a yellow solid (116.6 mg, 64 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1 H), 8.13 (d, *J* = 7.6 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.46 (s, 1 H), 7.42 (d, *J* = 7.2 Hz, 2 H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.21 (d, *J* = 7.2 Hz, 2 H), 6.76 (s, 1 H), 3.94 (s, 3 H), 2.43 (s, 3 H), 2.42 (s, 3 H), 1.46 (s, 3 H), 1.30 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 143.7, 141.0, 140.6, 140.0, 139.7, 139.3, 138.8, 138.2, 136.3, 135.6, 132.5, 131.9, 130.4, 129.9, 129.4, 129.4, 128.3, 125.3, 123.7, 120.4, 119.0, 118.8, 102.5, 92.4, 52.0, 29.8, 21.9, 21.8, 21.5, 21.4 ppm. ESI-HRMS: calcd. for $C_{34}H_{29}O_2$ $[M + H]^+$ 469.2162; found 469.2166.

(*E*)-Methyl 9-[1,3-Bis(4-methoxyphenyl)prop-2-yn-1-ylidene]-6,8-dimethyl-9*H*-fluorene-2-carboxylate (6i): By the general procedure for **5a**, **6i** was obtained as yellow solid (146.0 mg, 75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.65 (s, 1 H), 8.11–8.08 (m, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.73–7.71 (m, 2 H), 7.45 (s, 1 H), 7.44–7.42 (m, 2 H), 6.95 (d, *J* = 8.8 Hz, 1 H), 6.90 (d, *J* = 8.8 Hz, 2 H), 6.74 (s, 1 H), 3.91 (s, 3 H), 3.87 (s, 3 H), 3.85 (s, 3 H), 2.40 (s, 3 H), 1.48 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 160.4, 159.6, 143.6, 140.9, 139.8, 139.5, 138.5, 136.4, 135.3, 135.0, 133.6, 132.5, 131.8, 129.6, 128.8, 125.1, 123.6, 118.9, 118.7, 115.5, 114.3, 114.1, 102.6, 92.0, 55.5, 55.4, 52.0, 21.9, 21.5 ppm. ESI-HRMS: calcd. for $C_{34}H_{29}O_4$ $[M + H]^+$ 501.2060; found 501.2057.

2-Iodo-2′-(*p*-tolylethynyl)-1,1′-biphenyl (7):[13a] To **1a** (5.0 g, 11.7 mmol) were added Na_2CO_3 (3.71 g, 35.0 mmol), CuI (444.8 mg, 2.3 mmol), $Pd(PPh_3)_2Cl_2$ (819.7 mg, 1.2 mmol), and PPh_3 (918.9 mg, 3.5 mmol). The reaction vessel was evacuated and backfilled with Ar three times, and a solution of **2a** (1.75 mL, 14.0 mmol) in DMF (200.0 mL) was added with a syringe. The reaction mixture was stirred at 15–20 °C under an Ar atmosphere overnight (15 h). The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (100 mL × 2) and brine (100 mL) successively, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/PE 1:500) to give **7** (3.22 g, 70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 0.8, *J* = 7.2 Hz, 1 H), 7.66–7.64 (m, 1 H), 7.47–7.38 (m, 4 H), 7.32–7.29 (m, 1 H), 7.13–7.08 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 146.0, 139.0, 138.3, 132.9, 131.7, 131.4, 130.5, 129.6, 129.1, 128.0, 127.9, 127.8, 123.2, 120.3, 99.7, 93.5, 87.9, 21.6 ppm.

General Procedure for the Synthesis of 8 (Exemplified by 8a): To **7** (100 mg, 253.7 μmol) were added Na_2CO_3 (67.2 mg, 634.1 μmol), $Pd(PPh_3)_2Cl_2$ (17.8 mg, 25.4 μmol), PPh_3 (20.0 mg, 76.1 μmol), and CuI (9.66 mg, 50.73 μmol). The reaction vessel was evacuated and backfilled with argon three times, and a solution of phenylacetylene (47.0 μL, 507.3 μmol) in DMF (5.0 mL) was added with a syringe. The reaction mixture was stirred at 35 °C under an Ar atmosphere for 15 h. The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (10 mL × 2) and brine (10 mL) successively, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/PE 1:20) to give a yellow solid 9-[3-phenyl-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (**8a**; 68.2 mg, 73 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 6.4 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 1 H), 7.61–7.56 (m, 2 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.44–7.38 (m, 5 H), 7.33 (d, *J* = 7.6 Hz, 2 H), 7.24–7.22 (m, 1 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 6.63 (d, *J* = 8.0 Hz, 1 H), 2.50 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 140.4, 140.2, 138.5, 138.4, 137.8, 137.1, 131.8, 129.8, 129.1, 128.9, 128.8, 128.6, 128.5, 127.5, 126.7, 126.1, 125.7, 125.0, 123.5, 123.2, 119.5, 102.1, 92.4, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{21}$ $[M + H]^+$ 369.1643; found 369.1639.

9-[3-(*m*-Tolyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8b): By the general procedure for **8a**, **8b** was obtained as a yellow solid (63.1 mg, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90–8.88 (m, 1 H), 7.73–7.71 (m, 1 H), 7.65 (d, *J* = 7.6 Hz, 1 H), 7.47–7.45 (m, 2 H), 7.39–7.38 (m, 4 H), 7.31–7.29 (m, 2 H), 7.24–7.16 (m, 3 H), 6.90 (t, *J* = 8.0 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 1 H), 2.47 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 140.4, 140.0, 138.4, 138.3, 137.8, 137.2, 132.3, 129.9, 129.8, 129.1, 128.9, 128.8, 128.5, 128.4, 127.5, 126.7, 125.6, 125.0, 123.4, 123.3, 119.5, 119.5, 102.4, 92.0, 21.6, 21.4 ppm. ESI-HRMS: calcd. for $C_{30}H_{23}$ $[M + H]^+$ 383.1794; found 383.1790.

9-{3-[4-(*tert*-Butyl)phenyl]-1-(*p*-tolyl)prop-2-yn-1-ylidene}-9*H*-fluorene (8c): By the general procedure for **8a**, **8c** was obtained as a yellow solid (73.2 mg, 68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96–8.94 (m, 1 H), 7.77–7.75 (m, 1 H), 7.70 (d, *J* = 7.6 Hz, 1 H), 7.56–7.50 (m, 4 H), 7.46–7.41 (m, 4 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.27–7.24 (m, 1 H), 6.97–6.92 (m, 1 H), 6.67 (d, *J* = 8.0 Hz, 1 H), 2.51 (s, 3), 1.38 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 140.4, 140.4, 139.9, 138.5, 138.4, 137.9, 137.2, 131.6, 129.8, 129.1, 128.8, 128.3, 127.4, 126.7, 125.7, 125.6, 125.0, 123.6, 120.5, 119.5, 119.5, 102.5, 91.9, 35.0, 31.3, 21.6 ppm. ESI-HRMS: calcd. for $C_{33}H_{29}$ $[M + H]^+$ 425.2269; found 425.2272.

9-[3-(4-Fluorophenyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8d): By the general procedure for **8a**, **8d** was obtained as a yellow solid (73.5 mg, 75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69–8.66 (m, 1 H), 7.59–7.57 (m, 1 H), 7.51 (d, *J* = 7.6 Hz, 1 H), 7.40 (s, 1 H), 7.33–7.31 (m, 3 H), 7.28–7.25 (m, 2 H), 7.21–7.15 (m, 4 H), 7.09 (t, *J* = 7.2 Hz, 1 H), 6.77 (t, *J* = 7.6 Hz, 1 H), 6.47 (d, *J* = 7.6 Hz, 1 H), 2.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 140.5, 140.5, 138.6, 138.2, 137.7, 136.8, 134.5, 131.5, 129.9, 129.8, 129.1, 129.1, 129.0, 128.7, 127.5, 126.8, 125.7, 125.1, 124.9, 122.5, 119.6, 100.2, 93.2, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{20}F$ $[M + H]^+$ 387.1544; found 387.1540.

9-[3-(3-Fluorophenyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8e): By the general procedure for **8a**, **8e** was obtained as a yellow solid (82.3 mg, 84 %, yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.91–8.89 (m, 1 H), 7.75–7.73 (m, 1 H), 7.60–7.57 (d, *J* = 7.6 Hz, 1 H), 7.49–7.47 (d, *J* = 8.0 Hz, 2 H), 7.43–7.38 (m, 3 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 7.24–7.22 (m, 1 H), 6.95–6.90 (m, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 2.50 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 161.3, 140.8, 140.5, 140.5, 138.5, 138.2, 137.7, 136.8, 130.2, 130.1, 129.9, 129.1, 129.0, 128.6, 127.6, 127.6, 127.5, 126.8, 125.7, 125.3, 125.2, 124.9, 122.6, 119.6, 118.5, 118.3, 116.3, 116.1, 100.4, 93.0, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{20}F$ $[M + H]^+$ 387.1544; found 387.1548.

9-[3-(4-Chlorophenyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8f): By the general procedure for **8a**, **8f** was obtained as a yellow solid (69.5 mg, 68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72–8.69 (m, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.39–7.32 (m, 4 H), 7.31–7.28 (m, 2 H), 7.24–7.20 (m, 4 H), 7.15–7.11 (m, 1 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 2.38 (s, 3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 140.5, 138.5, 138.3, 137.7, 136.9, 135.0, 133.8, 132.9, 129.9, 129.0, 129.0, 128.6, 127.5, 126.8, 126.1, 125.7, 124.9, 122.8, 121.9, 119.6, 100.7, 100.1, 93.1, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{20}Cl$ $[M + H]^+$ 403.1248; found 403.1243.

9-[3-(3-Chlorophenyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8g): By the general procedure for **8a**, **8g** was obtained as a yellow solid (72.6 mg, 71 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76–8.74 (m, 1 H), 7.66–7.64 (m, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.47 (s, 1 H), 7.40–7.38 (m, 3 H), 7.36–7.32 (m, 2 H), 7.36 (s, 1 H), 7.24–7.22 (m, 1 H), 7.17 (t, *J* = 7.2 Hz, 1 H), 6.85 (t, *J* = 15.2 Hz, 1 H), 6.54 (d, *J* = 7.6 Hz, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 140.5, 140.5, 138.6, 138.2, 137.7, 136.8, 134.5, 131.5, 129.9, 129.8, 129.1, 129.1, 129.0, 128.7, 127.5, 126.8, 125.7, 125.1, 124.9, 122.5, 119.6, 100.2, 93.2, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{20}Cl$ [M + H]$^+$ 403.1248; found 403.1242.

9-[3-(4-Nitrophenyl)-1-(*p*-tolyl)prop-2-yn-1-ylidene]-9*H*-fluorene (8h): By the general procedure for **8a**, **8h** was obtained as a yellow solid (87.0 mg, 83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, *J* = 7.2 Hz, 1 H), 8.23 (d, *J* = 8.8 Hz, 2 H), 7.72 (d, *J* = 7.6 Hz, 1 H), 7.68 (s, 1 H), 7.66 (s, 1 H), 7.46–7.42 (m, 3 H), 7.41–7.35 (m, 2 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 7.23 (d, *J* = 13.2 Hz, 1 H), 6.93–6.89 (m, 1 H), 6.57 (d, *J* = 8.0 Hz, 1 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3, 142.1, 140.8, 140.7, 138.8, 138.0, 137.5, 136.4, 132.4, 130.2, 130.0, 129.5, 129.1, 129.0, 127.6, 127.0, 125.9, 124.9, 123.9, 121.7, 119.8, 119.7, 99.2, 97.0, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_20NO_{22}$ [M + H]$^+$ 414.1483; found 141.1479.

3-[3-(9*H*-Fluoren-9-ylidene)-3-(*p*-tolyl)prop-1-yn-1-yl]aniline (8i): By the general procedure for **8a**, **8i** was obtained as a yellow solid (66.1 mg, 68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90–8.88 (m, 1 H), 7.74–7.73 (m, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H), 7.48–7.46 (m, 1 H), 7.41–7.40 (m, 2 H), 7.32–7.31 (m, 2 H), 7.26–7.22 (m, 1 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 7.01 (d, *J* = 7.2 Hz, 1 H), 6.94–6.89 (d, 2 H), 6.71 (d, *J* = 7.2 Hz, 1 H), 6.62 (d, *J* = 7.6 Hz, 1 H), 3.56 (s, 2 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 140.4, 140.3, 140.0, 138.4, 137.8, 137.2, 129.8, 129.6, 129.1, 128.8, 128.4, 127.5, 126.7, 125.6, 125.0, 124.1, 123.4, 122.4, 119.5, 119.4, 118.0, 116.2, 102.5, 91.8, 21.6 ppm. ESI-HRMS: calcd. for $C_{29}H_{22}N$ [M + H]$^+$ 384.1747; found 384.1742.

General Procedure for the Synthesis of 9 (Exemplified by 9a): To **7** (200 mg, 507.3 μmol) were added Na_2CO_3 (161.3 mg, 1.5 mmol), $Pd(OAc)_2$ (11.4 mg, 50.7 μmol), and PPh_3 (39.9 mg, 152.2 μmol). The reaction vessel was evacuated and backfilled with argon three times, and a solution of methyl acrylate (91.9 μL, 1.0 mmol) in DMF (5.0 mL) was added with a syringe. The reaction mixture was stirred under an Ar atmosphere and heated at 110 °C with an oil bath for 8 h. The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (10 mL × 2) and brine (10 mL) successively, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/PE 1:20) to give (*E*)-methyl 4-(9*H*-fluoren-9-ylidene)-4-(*p*-tolyl)but-2-enoate (**9a**) as a yellow solid (164.5 mg, 92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82–8.78 (m, 1 H), 7.97 (d, *J* = 6.8 Hz, 1 H), 7.73–7.71 (m, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.40–7.38 (m, 1 H), 7.37–7.34 (m, 1 H), 7.33–7.31 (m, 2 H), 7.21 (d, *J* = 7.2 Hz, 1 H), 7.19–7.17 (m, 2 H), 6.88–6.84 (m, 1 H), 6.15 (d, *J* = 8.0 Hz, 1 H), 5.73 (dd, *J* = 1.6, *J* = 13.6 Hz, 1 H), 3.80 (s, 3 H), 2.49 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 145.0, 141.3, 141.1, 140.7, 139.4, 138.7, 138.5, 137.7, 136.2, 134.0, 130.1, 129.8, 129.0, 128.7, 127.6, 127.0, 126.1, 125.1, 120.0, 119.5, 51.9, 21.6 ppm. ESI-HRMS: calcd. for $C_{25}H_{21}O_2$ [M + H]$^+$ 353.1536; found 353.1527.

(*E*)-9-(1,3-Di-*p*-tolylallylidene)-9*H*-fluorene (9b): By the general procedure for **9a**, **9b** was obtained as a yellow solid (173.6 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 15.6 Hz, 1 H), 8.06 (s, 1 H), 7.81 (s, 1 H), 7.70 (d, *J* = 7.2 Hz, 1 H), 7.43–7.38 (m, 4 H), 7.38–7.33 (m, 2 H), 7.33–7.28 (m, 2 H), 7.24–7.17 (m, 3 H), 6.95–6.85 (m, 1 H), 6.46 (d, *J* = 16.0 Hz, 1 H), 6.21–6.17 (m, 1 H), 2.54 (s, 3 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.5, 140.7, 140.0, 139.4, 138.6, 138.5, 138.2, 137.7, 137.6, 134.8, 134.7, 130.4, 129.9, 129.8, 129.7, 127.5, 127.2, 127.1, 127.0, 126.6, 126.2, 125.1, 119.9, 119.3, 21.6, 21.5 ppm. ESI-HRMS: calcd. for $C_{30}H_{25}$ [M + H]$^+$ 385.1956; found 385.1960.

(*E*)-4-[3-(9*H*-Fluoren-9-ylidene)-3-(*p*-tolyl)prop-1-en-1-yl]pyridine (9c): By the general procedure for **9a**, **9c** was obtained as a yellow solid (179.0 mg, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 2 H), 8.23 (d, *J* = 16.0 Hz, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.61–7.59 (m, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H), 7.24–7.22 (m, 2 H), 7.20 (s, 1 H), 7.19 (s, 1 H), 7.17–7.13 (m, 2 H), 7.10–7.09 (m, 2 H), 7.04 (t, *J* = 14.8 Hz, 1 H), 6.73 (t, *J* = 8.0 Hz, 1 H), 6.19 (d, *J* = 15.6 Hz, 1 H), 6.01 (d, *J* = 8.0 Hz, 1 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 144.5, 141.6, 141.0, 140.4, 139.0, 138.5, 138.1, 137.6, 136.8, 134.6, 134.2, 130.2, 130.0, 128.3, 127.9, 127.2, 126.8, 126.3, 125.4, 121.2, 120.0, 119.4, 21.6 ppm. ESI-HRMS: calcd. for $C_{28}H_{22}N$ [M + H]$^+$ 372.1747; found 372.1741.

5-[(9*H*-Fluoren-9-ylidene)(*p*-tolyl)methyl]-4-(*p*-tolyl)-1*H*-1,2,3-triazole (10): To **5a** (150 mg, 392.16 μmol) were added NaN_3 (50.99 mg, 784.32 μmol) and $RuCl_3$ (16.27 mg, 78.43 μmol). The reaction vessel was evacuated and backfilled with argon three times, and DMF (5.0 mL) was added with a syringe. The reaction mixture was stirred under an Ar atmosphere and heated at 100 °C with an oil bath for 12 h. The reaction mixture was then diluted with EtOAc (50 mL), washed with H_2O (10 mL × 2) and brine (10 mL) successively, dried with anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/PE 1:10) to give **10** as a light green solid (109.1 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.60 (m, 4 H), 7.29–7.27 (m, 1 H), 7.26–7.21 (m, 3 H), 7.10 (d, *J* = 7.6 Hz, 2 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.98–6.92 (m, 2 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 6.46 (d, *J* = 8.0 Hz, 1 H), 2.34 (s, 3 H), 2.24 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.8, 139.1, 138.7, 138.5, 138.0, 137.8, 136.8, 129.6, 129.5, 129.4, 128.7, 128.7, 127.5, 127.0, 126.8, 125.5, 124.3, 119.5, 119.5, 21.5, 21.3 ppm. ESI-HRMS: calcd. for $C_{30}H_{24}N_3$ [M + H]$^+$ 426.1965; found 426.1961.

CCDC 1411943 (for **6f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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