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Brönsted Acid-Mediated Intramolecular Cyclization of Biaryl Triazenes for the Synthesis of Fluorenes and 9,10-Dihydro-Phenanthrenes

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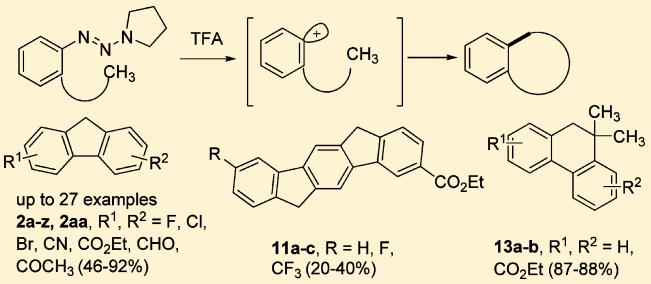
Supporting Information

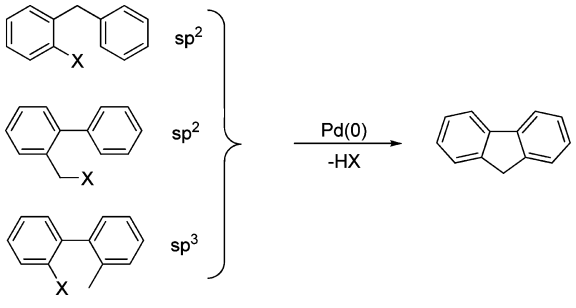
ABSTRACT: The efficient synthesis of fluorenes from biaryl triazenes is successfully developed. Up to 27 examples of biaryl triazenes are converted into their corresponding fluorene derivatives in the presence of CF_3COOH (4.0 equiv). Mechanism research indicates that the reaction undergoes concerted processes, and pentacoordinate carbocations may be involved in these reactions.



INTRODUCTION

The chemistry of polycyclic aromatic hydrocarbons (PAHs) has become a field of great interest during the past decades, especially in materials science because of their unique electrical and optical properties.[1] For example, the charge transport properties exhibited by some PAHs make them potential candidates for organic optoelectronic devices such as light-emitting diodes, field-effect transistors, and photovoltaics.[2] Fluorenes are notable structural motifs for the diverse PAH derivatives, since their broad application in many fields of optoelectronic materials, solar cells, biological, medical and so on, have been investigated for long time.[3] Several synthetic methods for preparing fluorenes have been well developed, especially the Pd-catalyzed cyclization via C−H bond activation with subsequent C−C bond formation for its simple operation and atom economy[4] (Scheme 1). However, these reactions are still limited because of harsh reaction condition, poor functional group tolerance or lacking regioselectivity. Thus, the development of conceptually practical approaches is still of great interest.

Scheme 1. Pd-Catalyzed C−H Activation for the Synthesis of Fluorenes



Meanwhile, the cyclization reaction initiated by the dediazotization of diazonium salts is a valuable reaction for the formation of fluorene derivatives from 2-alkylbiphenyl-2′-yl diazonium salts. Although the reaction has been reported for 70 years, because of the instability of diazonium salts, the reaction mechanism is still not clear[5] and the application is very limited. Compared to diazonium salts, triazenes,[6] namely, masked diazonium salts, offer many advantages owing to their stable property and compatibility with chemical reagents. Our group has extensive ongoing research in triazene chemistry[7] directed toward the synthesis of important heterocycles and PAHs. We have presented a comprehensive study of the carbocation-induced Friedel−Crafts arylation reaction of aryl triazenes that provides direct synthetic access to unsymmetrical and functionalized PAHs.[7b] Herein, we present a carbocation-induced cyclization of *o*-methyl biaryltriazenes and its application in the synthesis of the fluorenes and 9,10-dihydro-phenanthrenes (Scheme 2).

RESULTS AND DISCUSSION

As shown in Table 1, a number of starting material *o*-methyl biaryltriazenes **1** were successfully prepared from Suzuki−Miyaura cross-coupling between halo-triazene **A** and *o*-methyl phenyl boronic acid (for the synthesis of **1a−i**, **1aa**) or between triazene-boronic acid **B** and *o*-methyl phenyl halides (for the synthesis of **1j−z**) according to the previous reported procedure by Prof. Paul Knochel's and our groups.[8] Halo-triazene **A** and triazene-boronic acid **B** can be easily prepared from readily available aniline derivatives.[8]

With these starting materials in hand, we initially commenced our study by treating biaryl triazene **1a** with

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Scheme 2. Envisaged Carbocation-Induced Cyclization Reaction for the Synthesis of the Fluorenes

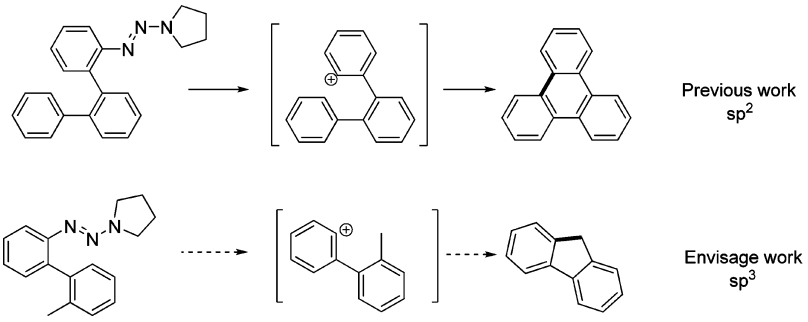
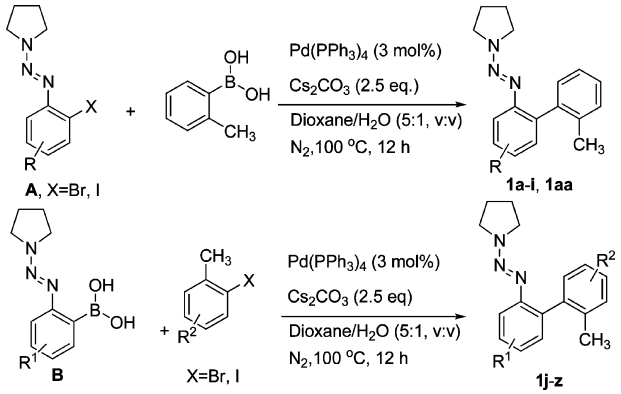
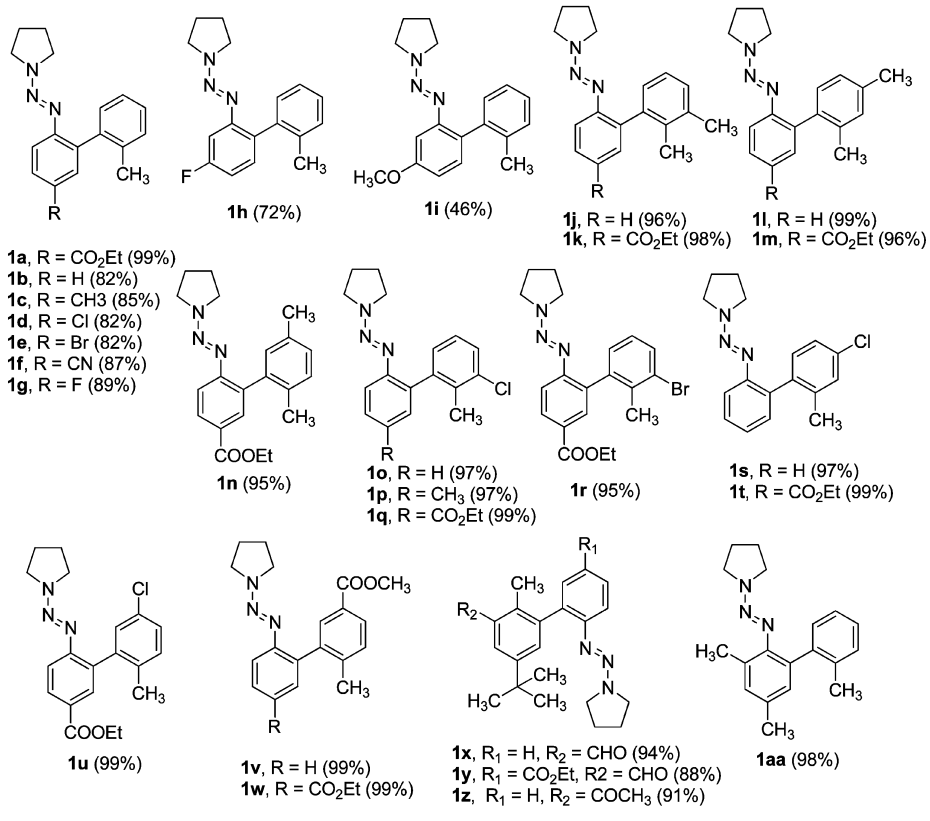


Table 1. Synthesis of Starting Material *o*-Methyl Biaryltriazenes[a,b,c]





[a]Reaction condition for **1a–i**, **1aa**: halo-triazene **A** (4.0 mmol), *o*-methyl phenyl boronic acid (4.8 mmol), $Pd(PPh_3)_4$ (0.12 mmol), Cs_2CO_3 (10 mmol) in dioxane/H_2O (v:v 5:1, 24 mL) at 100 °C for 12 h. [b]Reaction condition for **1j–z**: *o*-methyl phenyl halide (4.0 mmol), triazene-boronic acid **B** (4.8 mmol), $Pd(PPh_3)_4$ (0.12 mmol), Cs_2CO_3 (10 mmol) in dioxane/H_2O (v:v 5:1, 24 mL) at 100 °C for 12 h [c]Yield of the isolated product after flash column chromatograpy.

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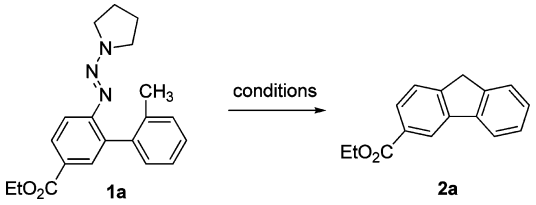
CF_3COOH (4.0 equiv) in THF at reflux condition. However, the starting material was fully recovered (Table 2, entry 1). The

Table 2. Screening of Reaction Conditions[a,b]



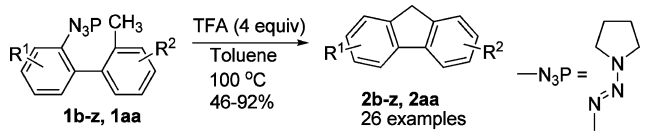
entry	acid	acid (equiv)	solvent	T (°C)	yield (%)
1	TFA	4.0	THF	70	0
2	TFA	4.0	DMF	70	<5
3	TFA	4.0	DMSO	70	<5
4	TFA	4.0	CH_3CN	70	35
5	TFA	4.0	CH_3OH	70	60
6	TFA	4.0	CH_2Cl_2	70	48
7	TFA	4.0	DCE	70	60
8	TFA	4.0	toluene	70	50
9	TFA	4.0	toluene	100	66
10	$BF_3{\cdot}Et_2O$	4.0	toluene	100	0
11	$BF_3{\cdot}Et_2O$	4.0	dioxane	100	67[c]
12	HOAc	4.0	toluene	100	0
13	*p*-TSA	4.0	toluene	100	13
14	TFA	1.0	toluene	100	29
15	TFA	2.0	toluene	100	44
16	TFA	3.0	toluene	100	51
17	TFA	5.0	toluene	100	67

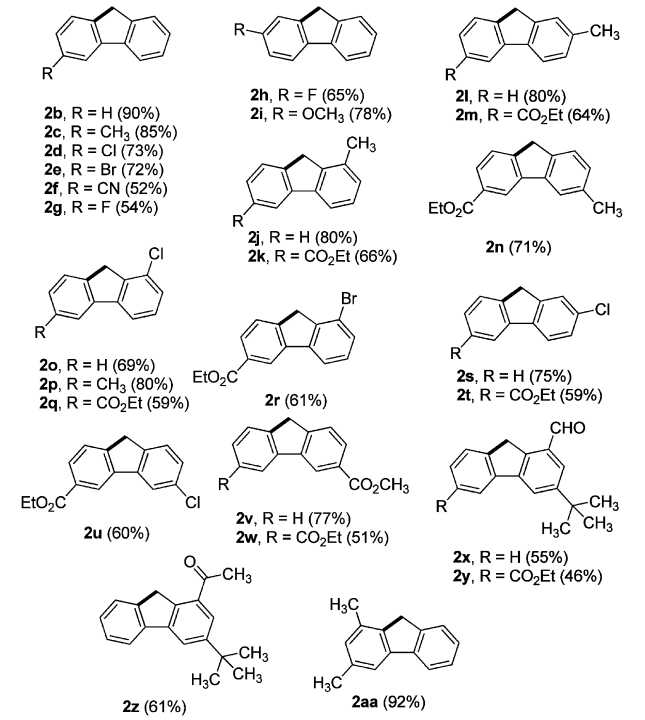
[a]All reactions were carried out with **1a**, acid, in solvent (5 mL) for 1−2 h. [b]Yield of the isolated product after flash column chromatography. [c]Mixture of cyclization product and fluoro-detriazenation product. TFA = trifluoroacetic acid; DMSO = dimethyl sulfoxide; DCE = 1,2-dichloroethane; *p*-TSA = *p*-toluenesulfonic acid.

desired cyclization product was isolated in less than 5% yield when the reaction was performed at 70 °C in DMF or DMSO (Table 2, entries 2 and 3). Also, we tried to increase the temperature to improve the yield, but failed. To our delight, when the other polar solvents CH_3OH and CH_3CN were applied, the yield was improved up to 60% (Table 2, entries 4 and 5). Further screening nonpolar solvents, such as CH_2Cl_2, DCE and toluene, revealed that the product **2a** was obtained in 48, 60 and 50% yields (Table 2, entries 6−8). Upon treatment of biaryl triazene **1a** with CF_3COOH in toluene at 100 °C, the yield of desired product **2a** increased to 66% (Table 2, entry 9). When the reaction was carried out using $BF_3{\cdot}OEt_2$ instead of CF_3COOH, the cyclization reaction occurred as well as the fluoro-detriazenation reaction (Table 2, entry 11). The other Brönsted acids such as HOAc, *p*-TSA were applied to this reaction; however, the reaction only gave the product in the poor yields (Table 2, entries 12, 13). The ratios of CF_3COOH affected the yields of the product, and using 4 equiv of TFA is a necessity (Table 2, entries 14−17). Thus, we were able to define the best conditions for this transformation: the reaction was carried out in the presence of CF_3COOH (4.0 equiv) at 100 °C in toluene.

With the optimized conditions in hand, the scope of the carbocation-induced cyclization was further investigated, and the results are summarized in Table 3. Both electron-rich and electron-deficient biaryl triazenes afforded the desired products in 52−90% yields (Table 3, **2b−i**). The substrates bearing

Table 3. Scope of the Synthesis of Functionalized 9*H*-Fluorenes from Biaryl triazenes[a,b]





[a]All reactions were carried out with biaryl triazenes (1.0 mmol), TFA (4.0 mmol) in toluene (5.0 mL) at 100 °C for 1 h. [b]Yield of the isolated product after flash column chromatograpy.

electron-donating groups on the aryl triazene motif showed higher reactivity and gave higher yield than the electron-withdrawing ones (Table 3, **2c** and **2f**; **2h** and **2i**; **2j** and **2k**; **2o−q**). The electronic nature of the substituents on the toluene motif also influenced the yield of the transformation. A decrease in yield was observed (Table 3, **2n**, **2u**, and **2w**; **2j**, **2o**, and **2x**), as the electron-donating ability in the toluene motif weakened. Moreover, the hindrance of substituents on the aromatic ring of **1** have little effect on this reaction (Table 3, **2k**, **2m**, and **2n**; **2q**, **2t**, and **2u**). Sterically hindered substrates (Table 3, **2z** and **2aa**) can also be converted to the corresponding fluorenes in 61−92% yields. Notably, the reaction of the bromine containing biaryl triazenes gave the product (Table 3, **2e** and **2r**) with bromine maintained. The bromine is attractive functional group for further elaboration. Functional groups, such as carbonyl group of ketone (Table 3, **2z**) and aldehyde (Table 3, **2x** and **2y**), ester (Table 3, **2i**, **2k**, **2m**, **2n**, **2q**, **2r**, **2t−w**, **2y**), cyano (Table 3, **2f**) can be tolerated in this cyclization reaction.

To probe the reaction mechanism, a radical inhibition test was performed under the standard reaction conditions. The reaction of **1a** with TFA proceeded smoothly under N_2 or O_2 (a well-known radical scavenger) to give **2a** in 64 and 66% yield, respectively. When classical radical scavengers such as 2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO), di(phenyl)-

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(2,4,6-trinitrophenyl)iminoazanium (DPPH) and 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy (galvinoxyl free radical) were added to the reaction system, respectively, the yield of the reaction was not affected (Figure 1). The results strongly suggest that the reaction does not proceed via a radical intermediate and the cation mechanism is probable.

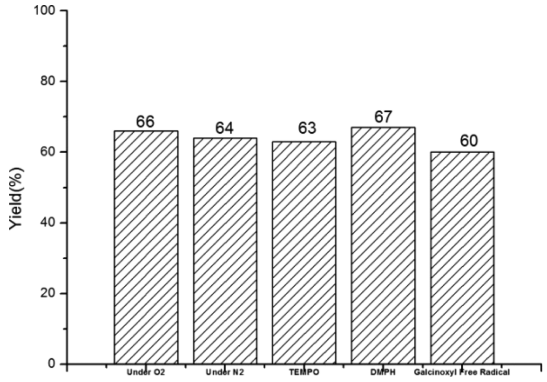


Figure 1. Influence of different radical scavengers. TEMPO = 2,2,6,6-tetramethyl-piperidin-1-yl)oxyl, DPPH = di(phenyl)-(2,4,6-trinitrophenyl)iminoazanium, galvinoxyl free radical = 2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylid.

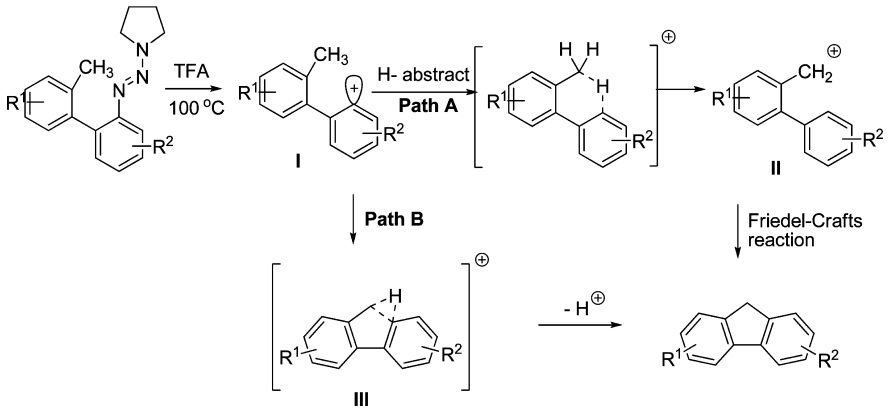
In principle, two carbocation mechanisms are conceivable for the results described in Scheme 3. In mechanism path **A**, the aryl cation intermediate **I** undergoes a rapid [1,5]-H shift[9] to form a more stable benzylic cation intermediate **II** followed by intramolecular Friedel–Crafts reaction to afford the cyclic product. In 1978, Heaney reported the intramolecular cyclization of 2-alkylbiphenyl-2′-yldiazonium salts and showed some evidence of pentacoordinate carbon species.[5c] Thus, the involvement of pentacoordinate carbocation is also possible. In mechanism path B, with the C–H functionalization,[10] the pentacoordinate carbocation[11] intermediate **III** is formed, and then the loss of proton gives cyclic compounds.

In order to distinguish between these two mechanisms, the deuterated experiments were carried out (Scheme 4). It was expected that the reaction of **1c**-d_3 in the presence of TFA would give a mixture of **2c**-d_2 and **2c**-d_3 if the intermediate **II** was formed (Scheme 3). In fact, we found **1c**-d_3, which bears an electron donating group on the triazene ring, only gave the corresponding cyclization compound **2c**-d_2. In order to exclude the electronic effect on the regioselectivity of this reaction, the substrate **1a**-d_3, which bears an electron withdrawing group on the triazene ring, was further investigated, and also only the **2a**-d_2 was formed. All of the above results that are presented in the intermediate **II** was not formed in this reaction. Besides of the deuterated control reaction, substrate **3a** was designed to validate the mechanism. Obviously, when the intermediate **II** was formed, the reaction of **3a** should give a mixture of **4a** and **4a**′. Actually, only **4a** was isolated in 74% yield. Similarly, **4b**[12] was obtained in 73% yield when the electron donating group on the aromatic ring was changed to electron-withdrawn group. All the results support the mechanism path B, and the formation of the pentacoordinate carbocation intermediate **III** is favored.

In addition, the present cyclization method could be applied to the synthesis of unsymmetrical functionalized 6,12-dihydroindeno[1,2-*b*]fluorenes (**11a–c**, Scheme 5). Thus, treating 1,4-dibromo-2,5-dimethyl-benzene (**5**) with *n*-BuLi, the selective Br/Li exchange occurred and formed the monolithium intermediate. After transmetalation with $ZnBr_2$ and the Negishi coupling reaction with iodo-triazenes **6a–c**, the biaryl triazenes **7a–c** were obtained in 65–80% yield. The biaryl triazenes **7a–c** were converted to the corresponding cyclic compounds **8a–c** in 48–81% yield. After coupling with boronic acid (**9**), the resulting fluorene-triazenes **10a–c** were all successfully converted to the corresponding unsymmetrical functionalized 6,12-dihydroindeno[1,2-*b*]fluorenes **11a–c** in 20–40% yields (Scheme 5).

In order to further expand the application of the reaction, we tried some substrates beyond *o*-methyl biaryltriazenes. When we treated the *o*-ethyl biaryltriazenes **12a** with TFA under the standard reaction conditions, the cyclization occurred as well as the hydro elimination. The mixture of elimination product and cyclization product was obtained in 64% yield with the ratio of 3:5 (the ratio was identified by proton NMR). The reaction of *o*-benzyl biaryltriazenes **12d** under the standard condition gave an unknown mixture. When we treated the *tert*-butyl biphenyl triazene **12b** with TFA under the standard reaction conditions, the 9,9-dimethyl-9,10-dihydro-phenanthrene **13b** was obtained in 87% yield. When the electron-withdrawing group CO_2Et was introduced to the *tert*-butyl biphenyl triazene (**12c**), the cyclization reaction was also carried out well and provided the corresponding 9,10-dihydro-phenanthrene (**13c**) in 88% yield (Scheme 6).

Scheme 3. Plausible Reaction Mechanism



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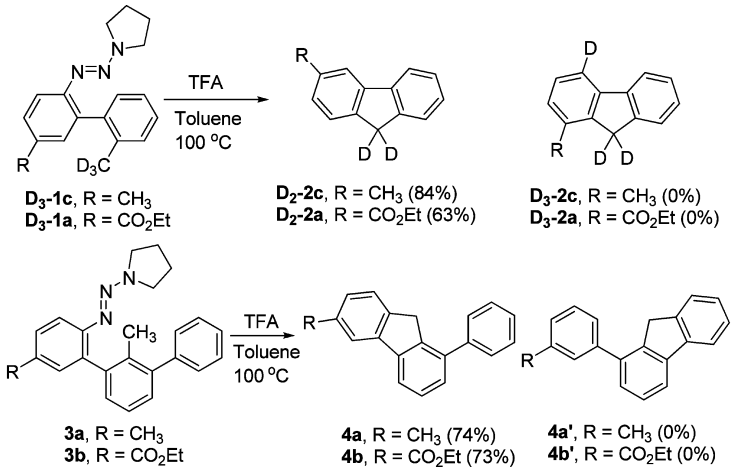
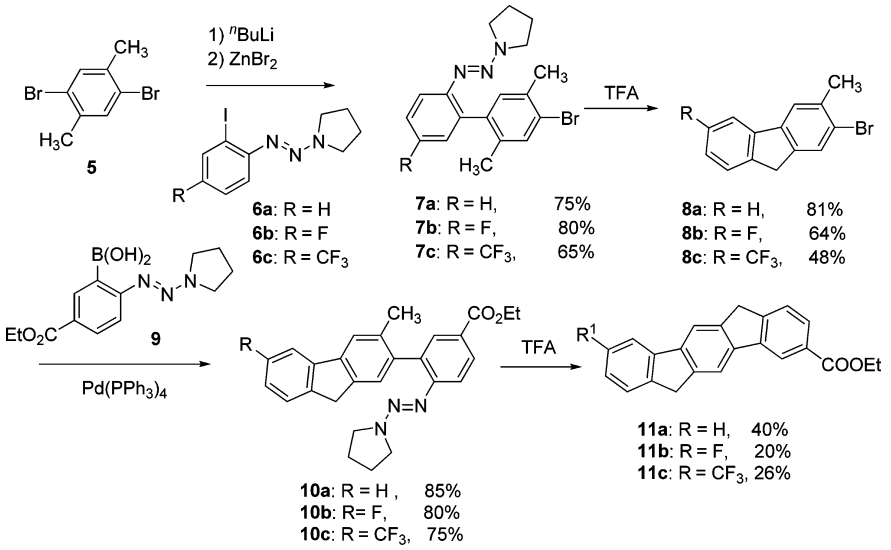
Scheme 4. Investigation of the Reaction Mechanism



Scheme 5. Synthesis of Unsymmetrical Functionalized 6,12-Dihydroindeno[1,2-*b*]fluorenes 11a−c



■ CONCLUSIONS

In summary, we have developed a carbocation-induced cyclization reaction to the efficient synthesis of a fused ring system from biaryl triazenes. The starting material was readily available from commercially available material with simple modification. Up to 27 examples of fluorene compounds are prepared in this new strategy. In addition, the unsymmetrical functionalized 6,12-dihydroindeno[1,2-*b*]fluorenes and 9,10-dihydro-phenanthrenes are achieved. Mechanism research indicates that the reaction undergoes concerted processes, and pentacoordinate carbocations may be involved in these reactions.

■ EXPERIMENTAL SECTION

A. General Information. Air- or moisture-sensitive reactions were carried out under nitrogen. THF and toluene were dried with sodium and freshly distilled. The other materials and solvents were purchased from commercial suppliers and used without additional purification unless otherwise stated. NMR spectra were recorded with 400 spectrometer using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR). Mass spectrometry data of the products were collected on a HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

B. General Procedure for Biaryl Triazenes. *B1. General Procedure for Compounds of* ***1a−1i*** *and* ***1aa.*** In a 50 mL Schlenck tube, substituted (*E*)-1-((2-halophenyl)diazenyl)pyrrolidine (1.0 equiv), *o*-tolylboronic acid (1.2 equiv), $Pd(PPh_3)_4$ (0.03 equiv) and Cs_2CO_3 (2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. On cooling the mixture to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.

*(E)-Ethyl 2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1a**).* Prepared from (*E*)-ethyl 3-iodo-4-(pyrrolidin-1-yldiazenyl)benzoate (1.603 g, 4.3 mmol) and *o*-tolylboronic acid (702 mg, 5.16 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1a** (1.556 g, 4.3 mmol, 99%) as a yellow solid: R_f = 0.57 (5:1 Petroleum ether/EtOAc); mp = 88−90 °C (recrystallized from EtOAc/Petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.8 Hz, 2.0 Hz, 1 H), 7.91 (d, J = 2.0 Hz, 1 H), 7.52 (d, J = 8.8 Hz, 1 H), 7.25−7.14 (m, 4 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.87 (br, 2 H), 3.29 (br, 2 H), 2.05 (s, 3 H), 1.92 (br, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.3, 140.0, 136.6, 136.3, 132.1, 130.0, 129.4, 129.1, 126.9, 126.4, 125.0, 116.5, 60.7, 50.9, 46.3, 23.8, 23.3, 20.3, 14.4; IR (ATR-FTIR) 1694, 1395, 1309, 1231, 1129, 858,

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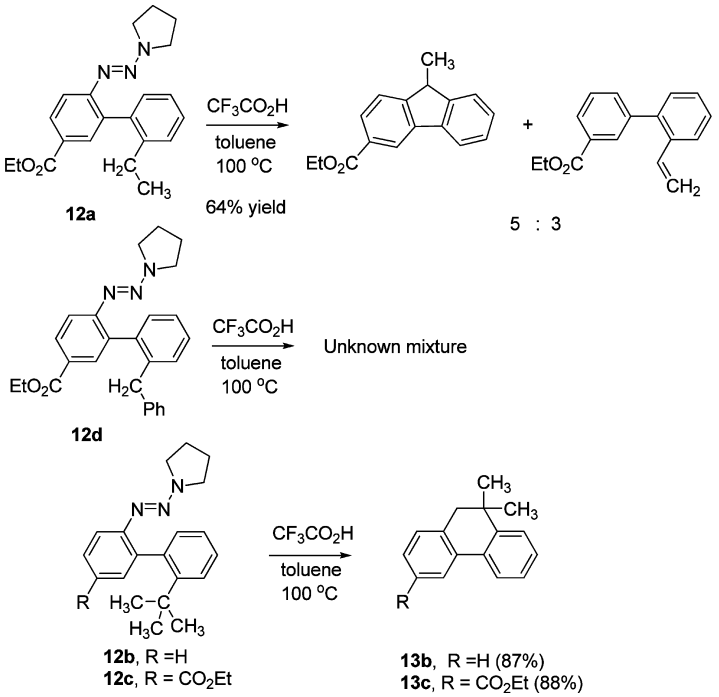
Scheme 6. Synthesis of 9,10-Dihydro-Phenanthrenes



770 cm^{-1}; MS (EI) *m/z* (%) 337 (M^+, 5), 177 (18), 165 (100), 149 (50), 121 (12), 103 (30), 76 (28), 41 (44); HRMS (EI-TOF) calcd for $C_{20}H_{23}N_3O_2$ (M^+) 337.1790, found 337.1797.

*(E)-1-((2′-Methyl-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**1b**).* Prepared from (*E*)-1-((2-iodophenyl)diazenyl)pyrrolidine (603 mg, 2 mmol) and *o*-tolylboronic acid (326 mg, 2.4 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1b** (432 mg, 1.6 mmol, 82%) as brown oil: R_f = 0.72 (5:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 1 H), 7.36–7.30 (m, 1 H), 7.24–7.16 (m, 6 H), 4.28–2.89 (m, 4 H), 2.14 (s, 3 H), 1.94–1.85 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 140.8, 136.6, 136.5, 130.5, 130.0, 129.0, 127.8, 126.6, 124.88, 124.86, 116.8, 23.6, 20.4; IR (ATR-FTIR) 1411, 1319, 1263, 1102, 856, 750 cm^{-1}; MS (EI) *m/z* (%) 265 (M^+, 7), 195 (11), 180 (18), 165 (100), 152 (49), 115 (10), 41 (27); HRMS (EI-TOF) calcd for $C_{17}H_{19}N_3$ (M^+) 265.1579, found 265.1584.

*(E)-1-((2′,5-Dimethyl-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**1c**).* Prepared from (*E*)-1-((2-iodo-4-methylphenyl)diazenyl)-pyrrolidine (630 mg, 2.0 mmol) and *o*-tolylboronic acid (326 mg, 2.4 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1c** (474 mg, 1.7 mmol, 85%) as a brown solid: R_f = 0.72 (5:1 Petroleum ether/EtOAc); mp = 50–51 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1 H), 7.24–7.18 (m, 4 H), 7.14 (d, *J* = 8.4 Hz, 1 H), 7.02 (s, 1 H), 3.55 (br, 4 H), 2.37 (s, 3 H), 2.15 (s, 3 H), 1.95–1.83 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.9, 136.6, 136.3, 134.4, 131.0, 130.0, 128.9, 128.5, 126.5, 124.8, 116.6, 23.7, 21.0, 20.4; IR (ATR-FTIR) 1413, 1316, 1262, 1107, 870, 758 cm^{-1}; MS (EI) *m/z* (%) 279 (M^+, 9), 195 (12), 181 (39), 165 (100), 152 (13), 41.1 (29); HRMS (EI-TOF) calcd for $C_{18}H_{21}N_3$ (M^+) 279.1735, found 279.1740.

*(E)-1-((5-Chloro-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1d**).* Prepared from (*E*)-1-((4-chloro-2-iodophenyl)-diazenyl)pyrrolidine (672 mg, 2.0 mmol) and *o*-tolylboronic acid (326 mg, 2.4 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1d** (493 mg, 1.6 mmol, 82%) as a yellow solid: R_f = 0.58 (10:1 Petroleum ether/EtOAc); mp = 57–58 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 1 H), 7.26 (dd, *J* = 9.2 Hz, 2.0 Hz, 1 H), 7.24–7.12 (m, 5 H), 3.81 (br, 2 H), 3.25 (br, 2 H), 2.12 (s, 3 H), 1.95–1.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 139.5, 137.9, 136.6, 130.2, 129.8, 129.1, 127.8, 127.0, 125.0, 118.0, 51.0, 46.2, 23.7, 23.6, 20.3; IR (ATR-FTIR) 1412, 1384, 1315, 1252, 1094, 821, 747, 640 cm^{-1}; MS (EI) *m/z* (%) 301 (M^+, Cl^{37}, 2), 299 (M^+, Cl^{35}, 5), 229 (8), 201 (7), 166 (87), 165 (100), 41 (26); HRMS (EI-TOF) calcd for $C_{17}H_{18}ClN_3$ (M^+) 299.1189, found 299.1186.

*(E)-1-((5-Bromo-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1e**).* Prepared from (*E*)-1-((4-bromo-2-iodophenyl)-diazenyl)pyrrolidine (1.122 g, 3.0 mmol) and *o*-tolylboronic acid (490 mg, 3.6 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1e** (832 mg, 2.4 mmol, 82%) as a yellow solid: R_f = 0.55 (10:1 Petroleum ether/EtOAc); mp = 54–56 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.6 Hz, 2.2 Hz, 1 H), 7.37–7.33 (m, 2 H), 7.25–7.14 (m, 4 H), 3.82 (br, 2 H), 3.26 (br, 2 H), 2.13 (s, 3 H), 1.95–1.82 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 139.4, 138.3, 136.6, 133.0, 130.7, 129.8, 129.1, 127.0, 125.0, 118.4, 117.7, 23.6, 23.4, 20.3; IR (ATR-FTIR) 1461, 1410, 1355, 1314, 1107, 819, 764, 684 cm^{-1}; MS (EI) *m/z* (%) 345 (M^+, Br^{81}, 4), 343 (M^+, Br^{79}, 5), 191 (15), 189 (11), 166 (100), 165 (92), 41 (33); HRMS (EI-TOF) calcd for $C_{17}H_{18}BrN_3$ (M^+) 343.0684, found 343.0691.

*(E)-2′-Methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carbonitrile (**1f**).* Prepared from (*E*)-3-iodo-4-(pyrrolidin-1-yldiazenyl)-benzonitrile (1.304 g, 4 mmol) and *o*-tolylboronic acid (653 mg, 4.8 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1f** (1.011 g, 3.5 mmol, 87%) as a yellow solid: R_f = 0.20 (10:1 Petroleum ether/EtOAc); mp = 82–84 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 2 H), 7.48 (d, *J* = 0.8 Hz, 1 H), 7.26–7.17 (m, 3 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 3.88 (br, 2 H), 3.28 (br, 2 H), 2.10 (s, 3 H), 1.94 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 138.7, 137.3, 136.5, 134.5, 131.7, 129.7, 129.2, 127.3, 125.2, 119.6, 117.3, 107.3, 51.1, 46.6, 23.8, 23.2, 20.3; IR (ATR-FTIR) 2213, 1476, 1377, 1307, 1129, 834, 759 cm^{-1}; MS (EI) *m/z* (%) 290 (M^+, 7), 220 (16), 205 (29), 190 (100), 177 (28), 165 (67), 152 (11), 70 (15), 41 (37); HRMS (EI-TOF) calcd for $C_{18}H_{18}N_4$ (M^+) 290.1531, found 290.1537.

*(E)-1-((5-Fluoro-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1g**).* Prepared from (*E*)-1-((4-fluoro-2-iodophenyl)-

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diazenyl)pyrrolidine (1.276 g, 4.0 mmol) and *o*-tolylboronic acid (653 mg, 4.8 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1g** (1.007 g, 3.6 mmol, 89%) as a brown solid: R_f = 0.52 (10:1 Petroleum ether/EtOAc); m.p = 84−85 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.40 (m, 1 H), 7.25−7.14 (m, 4 H), 7.02 (dt, J = 8.5 Hz, 2.4 Hz, 1 H), 6.93 (dd, J = 9.0 Hz, 2.6 Hz, 1 H), 3.54 (br, 4 H), 2.15 (s, 3 H), 1.95−1.83 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, $^1J_{C-F}$ = 242.0 Hz), 145.1 (d, $^4J_{C-F}$ = 2.7 Hz), 139.6, 138.0 (d, $^3J_{C-F}$ = 8.5 Hz), 136.5, 129.8, 129.1, 126.9, 125.0, 118.1 (d, $^3J_{C-F}$ = 8.5 Hz), 116.7 (d, $^2J_{C-F}$ = 21.8 Hz), 114.5 (d, $^2J_{C-F}$ = 21.6 Hz), 23.6, 20.3; IR (ATR-FTIR) 1473, 1395, 1309, 1255, 1166, 818, 762 cm^{-1}; MS (EI) m/z (%) 283 (M^+, 5), 213 (13), 198 (14), 183 (80), 170 (30), 165 (100), 41 (46); HRMS (EI-TOF) calcd for $C_{17}H_{18}FN_3$ (M^+) 283.1485, found 283.1489.

*(E)-1-((4-Fluoro-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1h**).* Prepared from (*E*)-1-((2-bromo-5-fluorophenyl)-diazenyl)pyrrolidine (1.088 g, 4.0 mmol) and *o*-tolylboronic acid (653 mg, 4.8 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1h** (812 mg, 2.9 mmol, 72%) as brown oil: R_f = 0.57 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.05 (m, 6 H), 6.79 (dt, J = 8.2 Hz, 2.4 Hz, 1 H), 3.77 (br, 2 H), 3.20 (br, 2 H), 2.05 (s, 3 H), 1.89−1.78 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{C-F}$ = 243.8 Hz), 150.2 (d, $^3J_{C-F}$ = 6.8 Hz), 140.0, 136.9, 132.6 (d, $^4J_{C-F}$ = 3.0 Hz), 131.5 (d, $^3J_{C-F}$ = 8.9 Hz), 130.2, 129.1, 126.8, 125.0, 111.5 (d, $^2J_{C-F}$ = 21.8 Hz), 103.4 (d, $^2J_{C-F}$ = 22.4 Hz), 50.7, 46.3, 23.7, 23.6, 20.4; IR (ATR-FTIR) 1595, 1476, 1411, 1341, 1313, 1091, 864, 763 cm^{-1}; MS (EI) m/z (%) 283 (M^+, 19), 213 (12), 198 (21), 183 (86), 165 (100), 157 (10), 133 (13), 41 (37); HRMS (EI-TOF) calcd for $C_{17}H_{18}FN_3$ (M^+) 283.1485, found 283.1487.

*(E)-1-((4-Methoxy-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1i**).* Prepared from (*E*)-1-((2-bromo-5-methoxyphenyl)-diazenyl)pyrrolidine (1.324 g, 4.0 mmol) and *o*-tolylboronic acid (653 mg, 4.8 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1i** (543 mg, 1.8 mmol, 46%) as a yellow solid: R_f = 0.35 (10:1 Petroleum ether/EtOAc); mp = 84−86 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 4 H), 7.13 (d, J = 8.0 Hz, 1 H), 7.06 (d, J = 2.4 Hz, 1 H), 6.79 (dd, J = 8.6 Hz, 2.6 Hz, 1 H), 4.15−2.97 (m, 7 H), 2.15 (s, 3 H), 1.98−1.83 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 149.5, 140.5, 136.9, 131.2, 130.4, 129.4, 129.0, 126.4, 124.8, 111.4, 101.2, 55.3, 23.6, 20.5; IR (ATR-FTIR) 1600, 1472, 1404, 1349, 1110, 858, 768 cm^{-1}; MS (EI) m/z (%) 295 (M^+, 10), 210 (29), 197 (92), 182 (66), 165 (100), 152 (68), 139 (18), 115 (24), 70 (12), 41 (44); HRMS (EI-TOF) calcd for $C_{18}H_{21}N_3O$ (M^+) 295.1685, found 295.1689.

*(E)-1-((2′,3,5-Trimethyl-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**1aa**).* Prepared from (*E*)-1-((2-bromo-4,6-dimethylphenyl)diazenyl)-pyrrolidine (1.410 g, 5.0 mmol) and *o*-tolylboronic acid (816 mg, 6.0 mmol) according to the general procedure **B1**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1aa** (1.444 g, 4.9 mmol, 98%) as brown oil: R_f = 0.59 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.08 (m, 4 H), 7.02 (s, 1 H), 6.85 (s, 1 H), 3.45−3.28 (m, 4 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 2.06 (s, 3 H), 1.83−1.74 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 141.6, 135.8, 134.1, 133.6, 130.6, 130.33, 130.28, 128.8, 128.6, 126.0, 124.7, 47.9, 23.7, 20.8, 20.3, 18.3; IR (ATR-FTIR) 1427, 1322, 1211, 1116, 859, 758 cm^{-1}; MS (EI) m/z (%) 293 (M^+, 13), 209 (7), 195 (48), 180 (92), 165 (100), 152 (21), 105 (12), 41 (44); HRMS (EI-TOF) calcd for $C_{19}H_{23}N_3$ (M^+) 293.1892, found 293.1897.

*B2. General Procedure for Compounds of **1j**−**1z**.* In a 50 mL Schlenck tube, substituted 1-halo-2-methylbenzene (1.0 equiv), triazenylphenylboronic acid (1.2 equiv), $Pd(PPh_3)_4$ (0.03 equiv) and Cs_2CO_3 (2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v), the tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. On cooling the mixture to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.

*(E)-1-((2′,3′-Dimethyl-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**1j**).* Prepared from 1-iodo-2,3-dimethylbenzene (928 mg, 4 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl) phenyl)boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1j** (1.070 g, 3.8 mmol, 96%) as brown oil: R_f = 0.57 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 1 H), 7.33 (t, J = 7.2 Hz, 1 H), 7.24−7.16 (m, 2 H), 7.15−7.05 (m, 3 H), 3.57 (br, 4 H), 2.33 (s, 3 H), 2.03 (s, 3 H), 1.96−1.85 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 140.7, 137.0, 135.8, 135.1, 130.6, 128.1, 128.0, 127.7, 124.9, 124.4, 116.9, 23.7, 20.5, 17.1; IR (ATR-FTIR) 1411, 1319, 1211, 1101, 754 cm^{-1}; MS (EI) m/z (%) 279 (M^+, 13), 209 (12), 194 (18), 181 (51), 165 (100), 152 (18), 41 (13); HRMS (EI-TOF) calcd for $C_{18}H_{21}N_3$ (M^+) 279.1735, found 279.1739.

*(E)-Ethyl 2′,3′-dimethyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1k**).* Prepared from 1-iodo-2,3-dimethylbenzene (928 mg, 4.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.397 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1k** (1.375 g, 3.9 mmol, 98%) as a yellow solid: R_f = 0.33 (10:1 Petroleum ether/EtOAc); mp = 129−131 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1 H), 7.92 (d, J = 1.2 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 1 H), 7.19−7.00 (m, 3 H), 4.36 (q, J = 7.2 Hz, 2 H), 3.87 (br, 2 H), 3.29 (br, 2 H), 2.32 (s, 3 H), 2.00 (s, 3 H), 1.92 (br, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.3, 140.0, 136.8, 135.9, 135.1, 132.3, 129.3, 128.4, 127.8, 126.3, 124.6, 116.5, 60.6, 50.9, 46.4, 23.8, 23.4, 20.5, 17.1, 14.3; IR (ATR-FTIR) 1695, 1597, 1394, 1306, 1232, 1130, 777 cm^{-1}; MS (EI) m/z (%) 351 (M^+, 31), 261 (43), 253 (43), 181 (100), 180 (100), 165 (100), 152 (30), 70 (14), 41 (21); HRMS (EI-TOF) calcd for $C_{21}H_{25}N_3O_2$ (M^+) 351.1947, found 351.1948.

*(E)-1-((2′,4′-Dimethyl-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**1l**).* Prepared from 1-iodo-2,4-dimethylbenzene (928 mg, 4 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl) phenyl)boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1l** (1.150 g, 4.0 mmol, 99%) as a yellow solid: R_f = 0.56 (10:1 Petroleum ether/EtOAc); mp = 62−64 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 1 H), 7.35−7.29 (m, 1 H), 7.23−7.16 (m, 2 H), 7.12 (d, J = 7.2 Hz, 1 H), 7.07−7.00 (m, 2 H), 3.59 (br, 4 H), 2.38 (s, 3 H), 2.13 (s, 3 H), 1.96−1.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 137.8, 136.5, 136.4, 136.0, 130.7, 130.0, 129.9, 127.7, 125.6, 124.9, 116.9, 23.7, 21.1, 20.4; IR (ATR-FTIR) 1474, 1402, 1340, 1266, 1100, 807, 757 cm^{-1}; MS (EI) m/z (%) 279 (M^+, 6), 194 (15), 181 (54), 178 (22), 165 (100), 152 (15), 41 (26); HRMS (EI-TOF) calcd for $C_{18}H_{21}N_3$ (M^+) 279.1735, found 279.1738.

*(E)-Ethyl 2′,4′-dimethyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1m**).* Prepared from 1-iodo-2,4-dimethylbenzene (464 mg, 2.0 mmol) and (E)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (699 mg, 2.4 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1m** (674 mg, 1.9 mmol, 96%) as a yellow solid: R_f = 0.28 (10:1 Petroleum ether/EtOAc); mp = 62−64 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.6 Hz, 1.8 Hz, 1 H), 7.90 (d, J = 2.0 Hz, 1 H), 7.50 (d, J = 8.4 Hz, 1 H), 7.09 (d, J = 7.2 Hz, 1 H), 7.05−6.99 (m, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.88 (br, 2 H), 3.32 (br, 2 H), 2.36 (s, 3 H), 2.09 (s, 3 H), 1.93 (br, 4 H), 1.37 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.4, 137.0, 136.43, 136.35, 136.28, 132.4, 129.94, 129.88, 129.3, 126.3, 125.7, 116.5, 60.7, 46.4, 23.8, 23.4, 21.1, 20.3, 14.3; IR (ATR-FTIR) 1698, 1393, 1306, 1230, 1102, 855, 712 cm^{-1}; MS (EI) m/z (%) 351 (M^+, 8), 294 (13), 253 (16), 207 (11), 181 (94), 165 (100), 152 (18), 77 (11), 41 (39);

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HRMS (EI-TOF) calcd for $C_{21}H_{25}N_3O_2$ (M^+) 351.1947, found 351.1944.

*(E)-Ethyl 2′,5′-dimethyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1n**).* Prepared from 2-iodo-1,4-dimethylbenzene (928 mg, 4.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.397 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1n** (1.329 g, 3.8 mmol, 95%) as a yellow solid: R_f = 0.33 (10:1 Petroleum ether/EtOAc); mp = 125−126 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1 H), 7.92 (s, 1 H), 7.52 (d, J = 8.4 Hz, 1 H), 7.12−7.01 (m, 3 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.88 (br, 2 H), 3.33 (br, 2 H), 2.34 (s, 3 H), 2.07 (s, 3 H), 1.93 (br, 4 H), 1.39 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.3, 139.8, 136.5, 134.3, 133.6, 132.2, 130.6, 129.3, 128.9, 127.6, 126.4, 116.4, 60.6, 46.4, 23.7, 20.9, 19.8, 14.3; IR (ATR-FTIR) 1696, 1395, 1309, 1232, 1105, 809, 767 cm^{-1}; MS (EI) m/z (%) 351 (M^+, 5), 266 (21), 207 (12), 181 (99), 165 (100), 149 (47), 103 (26), 76 (21), 41 (38); HRMS (EI-TOF) calcd for $C_{21}H_{25}N_3O_2$ (M^+) 351.1947, found 351.1950.

*(E)-1-((3′-Chloro-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1o**).* Prepared from 1-chloro-3-iodo-2-methylbenzene (1.010 g, 4.0 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl)phenyl)-boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1o** (1.162 g, 3.9 mmol, 97%) as brown oil: R_f = 0.61 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 1 H), 7.38−7.30 (m, 2 H), 7.23−7.17 (m, 2 H), 7.16−7.11 (m, 2 H), 4.09−3.12 (m, 4 H), 2.16 (s, 3 H), 1.97−1.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 142.8, 135.9, 134.9, 134.1, 130.2, 128.6, 128.2, 127.4, 125.7, 124.9, 116.9, 23.7, 18.0; IR (ATR-FTIR) 1410, 1318, 1266, 1104, 854, 755 cm^{-1}; MS (EI) m/z (%) 301 (M^+, Cl^{37}, 7), 299 (M^+, Cl^{35}, 21), 229 (14), 201 (18), 180 (22), 166 (100), 165 (100), 152 (35), 115 (12), 70 (13), 41 (41); HRMS (EI-TOF) calcd for $C_{17}H_{18}ClN_3$ (M^+) 299.1189, found 299.1194.

*(E)-1-((3′-Chloro-2′,5-dimethyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1p**).* Prepared from 1-chloro-3-iodo-2-methylbenzene (504 mg, 2.0 mmol) and (*E*)-(5-methyl-2-(pyrrolidin-1-yldiazenyl)-phenyl)boronic acid (559 mg, 2.4 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1p** (607 mg, 1.9 mmol, 97%) as a brown solid: R_f = 0.56 (10:1 Petroleum ether/EtOAc); mp = 95−97 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 1 H), 7.33−7.30 (m, 1 H), 7.15 (d, J = 8.0 Hz, 1 H), 7.13−7.08 (m, 2 H), 6.99 (s, 1 H), 3.55 (br, 4 H), 2.37 (s, 3 H), 2.15 (s, 3 H), 1.97−1.83 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 142.9, 135.7, 134.9, 134.5, 134.1, 130.8, 128.9, 128.5, 127.3, 125.7, 116.7, 23.7, 20.9, 18.0; IR (ATR-FTIR) 1415, 1348, 1316, 1267, 1124, 824, 742 cm^{-1}; MS (EI) m/z (%) 315 (M^+, Cl^{37}, 1), 313 (M^+, Cl^{35}, 4), 194 (11), 180 (87), 165 (100), 152 (15), 56 (23), 41 (92); HRMS (EI-TOF) calcd for $C_{18}H_{20}ClN_3$ (M^+) 313.1346, found 313.1342.

*(E)-Ethyl 3′-chloro-2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1q**).* Prepared from 1-chloro-3-iodo-2-methylbenzene (504 mg, 2.0 mmol) and (E)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (699 mg, 2.4 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1q** (734 mg, 2.0 mmol, 99%) as a yellow solid: R_f = 0.26 (10:1 Petroleum ether/EtOAc); mp = 114−115 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 8.6 Hz, 2.2 Hz, 1 H), 7.88 (d, J = 2.0 Hz, 1 H), 7.53 (d, J = 8.4 Hz, 1 H), 7.33 (dd, J = 7.2 Hz, 2.0 Hz, 1 H), 7.17−7.07 (m, 2 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.88 (br, 2 H), 3.29 (br, 2 H), 2.12 (s, 3 H), 1.94 (br 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 152.2, 141.9, 135.6, 134.9, 134.1, 131.9, 129.8, 128.5, 127.7, 126.3, 125.8, 116.4, 60.7, 51.0, 46.4, 23.8, 23.3, 17.9, 14.3; IR (ATR-FTIR) 1701, 1394, 1307, 1232, 1105, 859, 776 cm^{-1}; MS (EI) m/z (%) 373 (M^+, Cl^{37}, 3), 371 (M^+, Cl^{35}, 9), 227 (12), 201 (42), 165 (100), 139 (13), 119 (14), 91 (25), 70 (21), 41 (38); HRMS (EI-TOF) calcd for $C_{20}H_{22}ClN_3O_2$ (M^+) 371.1401, found 371.1411.

*(E)-Ethyl 3′-bromo-2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1r**).* Prepared from 1-bromo-3-iodo-2-methylbenzene (1.776 g, 6.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (2.095 g, 7.2 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1r** (2.372 g, 5.7 mmol, 95%) as a yellow solid: R_f = 0.39 (10:1 Petroleum ether/EtOAc); mp = 116−117 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.6 Hz, 1.8 Hz, 1 H), 7.87 (d, J = 2.0 Hz, 1 H), 7.56−7.50 (m, 2 H), 7.14 (dd, J = 7.6 Hz, 1.2 Hz, 1 H), 7.05 (t, J = 7.8 Hz, 1 H), 4.36 (q, J = 7.2 Hz, 2 H), 3.87 (br, 2 H), 3.29 (br, 2 H), 2.16 (s, 3 H), 1.94 (br, 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 152.2, 142.0, 136.6, 135.9, 131.8, 131.1, 129.8, 129.2, 126.4, 126.2, 125.1, 116.5, 60.7, 51.0, 46.4, 23.8, 23.4, 21.0, 14.4; IR (ATR-FTIR) 1701, 1397, 1307, 1231, 1105, 776, 711 cm^{-1}; MS (EI) m/z (%) 417 (M^+, Br^{81}, 5), 415 (M^+, Br^{79}, 5), 262 (65), 238 (41), 183 (55), 166 (100), 165 (100), 152 (17), 108 (14), 41 (15); HRMS (EI-TOF) calcd for $C_{20}H_{22}BrN_3O_2$ (M^+) 415.0895, found 415.0893.

*(E)-1-((4′-Chloro-2′-methyl-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**1s**).* Prepared from 4-chloro-1-iodo-2-methylbenzene (1.010 g, 4.0 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl)phenyl)-boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1s** (1.158 g, 3.9 mmol, 97%) as a yellow solid: R_f = 0.39 (10:1 Petroleum ether/EtOAc); mp = 84−86 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 1 H), 7.33 (t, J = 7.6 Hz, 1 H), 7.22−7.10 (m, 5 H), 4.11−3.02 (m, 4 H), 2.11 (s, 3 H), 1.95−1.86 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 139.3, 138.7, 135.3, 132.0, 131.3, 130.3, 128.8, 128.2, 124.9, 116.9, 23.7, 20.3; IR (ATR-FTIR) 1401, 1342, 1316, 1267, 1097, 867, 808, 759 cm^{-1}; MS (EI) m/z (%) 301 (M^+, Cl^{37}, 6), 299 (M^+, Cl^{35}, 18), 229 (40), 214 (14), 201 (38), 166 (100), 165 (100), 152 (28), 70 (17), 41 (39); HRMS (EI-TOF) calcd for $C_{17}H_{18}ClN_3$ (M^+) 299.1189, found 299.1182.

*(E)-Ethyl 4′-chloro-2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1t**).* Prepared from 4-chloro-1-iodo-2-methylbenzene (1.010 g, 4.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.397 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1t** (1.465 g, 3.9 mmol, 99%) as a light yellow solid: R_f = 0.28 (10:1 Petroleum ether/EtOAc); mp = 82−83 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.8 Hz, 1.6 Hz, 1 H), 7.85 (d, J = 2.0 Hz, 1 H), 7.52 (d, J = 8.4 Hz, 1 H), 7.22−7.14 (m, 2 H), 7.11 (d, J = 8.0 Hz, 1 H), 4.35 (q, J = 7.2 Hz, 2 H), 3.88 (br, 2 H), 3.30 (br, 2 H), 2.09 (s, 3 H), 1.94 (br, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 152.2, 138.7, 138.6, 135.1, 132.4, 132.0, 131.2, 129.7, 128.9, 126.4, 125.1, 116.5, 60.7, 46.5, 23.9, 23.3, 20.3, 14.3; IR (ATR-FTIR) 1699, 1393, 1306, 1230, 1130, 862, 776 cm^{-1}; MS (EI) m/z (%) 373 (M^+, Cl^{37}, 3), 371 (M^+, Cl^{35}, 7), 201 (35), 203 (10), 166 (67), 165 (100), 70 (11), 41 (28); HRMS (EI-TOF) calcd for $C_{20}H_{22}ClN_3O_2$ (M^+) 371.1401, found 371.1406.

*(E)-Ethyl 5′-chloro-2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1u**).* Prepared from 4-chloro-2-iodo-1-methylbenzene (1.008 g, 4.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.397 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1u** (1.487 g, 4.0 mmol, 99%) as a light yellow solid: R_f = 0.33 (10:1 Petroleum ether/EtOAc); mp = 124−125 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1 H), 7.87 (s, 1 H), 7.53 (d, J = 8.4 Hz, 1 H), 7.22−7.16 (m, 2 H), 7.12 (d, J = 8.4 Hz, 1 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.88 (br, 2 H), 3.30 (br, 2 H), 2.07 (s, 3 H), 1.93 (br, 4 H), 1.38 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 152.1, 141.7, 135.2, 134.9, 131.8, 130.4, 130.3, 129.8, 126.8, 126.4, 116.9, 116.5, 60.7, 46.4, 23.8,

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19.8, 14.3; IR (ATR-FTIR) 1697, 1393, 1309, 1230, 1107, 813, 755 cm^{-1}; MS (EI) *m/z* (%) 373 (M^+, Cl^{37}, 2), 371 (M^+, Cl^{35}, 6), 262 (18), 201 (55), 183 (36), 165 (100), 108 (12), 70 (23), 41 (35); HRMS (EI-TOF) calcd for $C_{20}H_{22}ClN_3O_2$ (M^+) 371.1401, found 371.1406.

*(E)-Methyl 6-methyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1v**).* Prepared from methyl 3-iodo-4-methylbenzoate (1.104 g, 4.0 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl)phenyl)-boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1v** (1.289 g, 4.0 mmol, 99%) as brown oil: R_f = 0.31 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.86 (m, 2 H), 7.46 (d, *J* = 8.4 Hz, 1 H), 7.36−7.30 (m, 1 H), 7.26 (d, *J* = 8.0 Hz, 1 H), 7.19−7.17 (m, 2 H), 4.22−2.86 (m, 7 H), 2.18 (s, 3 H), 1.94−1.81 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 148.6, 142.6, 141.0, 135.5, 131.3, 130.3, 129.1, 128.2, 127.8, 127.0, 125.0, 116.8, 51.8, 23.6, 20.7; IR (ATR-FTIR) 1716, 1409, 1311, 1236, 1106, 758 cm^{-1}; MS (EI) *m/z* (%) 323 (M^+, 7), 193 (17), 181 (13), 166 (93), 165 (100), 59 (27), 41 (22); HRMS (EI-TOF) calcd for $C_{19}H_{21}N_3O_2$ (M^+) 323.1634, found 323.1644.

*(E)-3-Ethyl 3′-methyl 6′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3,3′-dicarboxylate (**1w**).* Prepared from methyl 3-iodo-4-methylbenzoate (1.104 g, 4.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.397 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1w** (1.561 g, 3.9 mmol, 99%) as a yellow solid: R_f = 0.14 (10:1 Petroleum ether/EtOAc); mp = 110−111 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4 Hz, 1.6 Hz, 1 H), 7.95−7.84 (m, 3 H), 7.54 (d, *J* = 8.4 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 3.98−3.79 (bs, 5 H), 3.24 (br, 2 H), 2.17 (s, 3 H), 1.91 (br, 4 H), 1.38 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.6, 152.2, 142.5, 140.3, 135.3, 131.9, 131.1, 129.8, 129.2, 128.2, 127.1, 126.4, 116.4, 60.7, 51.8, 50.9, 46.4, 23.8, 23.3, 20.6, 14.3; IR (ATR-FTIR) 1713, 1600, 1391, 1309, 1253, 1106, 834, 755 cm^{-1}; MS (EI) *m/z* (%) 395 (M^+, 9), 277 (12), 262 (40), 193 (25), 183 (39), 165 (100), 149 (36), 70 (22), 59 (29), 41 (38); HRMS (EI-TOF) calcd for $C_{22}H_{25}N_3O_4$ (M^+) 395.1845, found 395.1839.

*(E)-5-(tert-Butyl)-2-methyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carbaldehyde (**1x**).* Prepared from methyl 5-(*tert*-butyl)-3-iodo-2-methylbenzaldehyde (1.209 g, 4.0 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1x** (1.314 g, 3.8 mmol, 94%) as brown oil: R_f = 0.32 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1 H), 7.82 (d, *J* = 1.6 Hz, 1 H), 7.51−7.25 (m, 2 H), 7.39−7.32 (m, 1 H), 7.24−7.18 (m, 2 H), 4.05−3.04 (m, 4 H), 2.40 (s, 3 H), 1.96−1.85 (m, 4 H), 1.34 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 148.9, 147.8, 142.3, 136.6, 135.5, 133.7, 133.5, 130.7, 128.3, 126.5, 124.9, 117.1, 34.4, 31.2, 23.6, 23.5, 15.8; IR (ATR-FTIR) 2869, 1688, 1473, 1409, 1318, 1097, 759 cm^{-1}; MS (EI) *m/z* (%) 349 (M^+, 6), 279 (11), 264 (33), 191 (18), 178 (32), 167 (66), 70 (25), 57 (100), 41 (56); HRMS (EI-TOF) calcd for $C_{22}H_{27}N_3O$ (M^+) 349.2154, found 349.2146.

*(E)-Ethyl 5′-(tert-butyl)-3′-formyl-2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**1y**).* Prepared from methyl 5-(*tert*-butyl)-3-iodo- 2-methylbenzaldehyde (907 mg, 3.0 mmol) and (*E*)-(5-(ethoxycarbonyl)-2- (pyrrolidin-1-yldiazenyl)phenyl) boronic acid (1.048 g, 3.6 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1y** (1.117 g, 2.7 mmol, 88%) as a yellow solid: R_f = 0.16 (10:1 Petroleum ether/EtOAc); mp = 125−127 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1 H), 8.02 (dd, *J* = 8.6 Hz, 1.4 Hz, 1 H), 7.89 (d, *J* = 1.6 Hz, 1 H), 7.82 (d, *J* = 1.6 Hz, 1 H), 7.55 (d, *J* = 8.8 Hz, 1 H), 7.46 (d, *J* = 1.6 Hz, 1 H), 4.37 (q, *J* = 7.2 Hz, 2 H), 3.87 (br, 2 H), 3.23 (br, 2 H), 2.37 (s, 3 H), 1.91 (br, 4 H), 1.38 (t, *J* = 7.0 Hz, 3 H), 1.34 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 166.6, 152.4, 148.0, 141.6, 136.5, 135.4, 133.5, 133.3, 132.2, 129.8, 126.9, 126.4, 116.6, 60.8, 34.5, 31.2, 15.7, 14.3; IR (ATR-FTIR) 2871, 1709, 1399, 1307, 1231, 1106, 841, 754 cm^{-1}; MS (EI) *m/z* (%) 421 (M^+, 4), 351 (22), 336 (40), 227 (30), 267 (32), 247 (35), 235 (20), 202 (28), 177 (60), 149 (100), 103 (72), 57 (100), 41 (43); HRMS (EI-TOF) calcd for $C_{25}H_{31}N_3O_3$ (M^+) 421.2365, found 421.2366.

*(E)-1-(5-(tert-Butyl)-2-methyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-yl)ethanone (**1z**).* Prepared from methyl 1-(5-(*tert*-butyl)-3-iodo-2-methylphenyl)ethanone (1.265 g, 4.0 mmol) and (*E*)-(2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid (1.051 g, 4.8 mmol) according to the general procedure **B2**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1z** (1.318 g, 3.6 mmol, 91%) as brown oil: R_f = 0.25 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.37−7.31 (m, 2 H), 7.22−7.17 (m, 2 H), 3.57 (br, 4 H), 2.61 (s, 3 H), 2.18 (s, 3 H), 1.93−1.87 (m, 4 H), 1.33 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 148.8, 147.0, 142.0, 139.1, 136.2, 132.3, 130.7, 130.6, 128.1, 124.8, 123.4, 117.2, 34.4, 31.3, 30.5, 23.6, 17.9; IR (ATR-FTIR) 2869, 1684, 1411, 1318, 1241, 1103, 759 cm^{-1}; MS (EI) *m/z* (%) 363 (M^+, 4), 278 (53), 209 (19), 191 (28), 178 (30), 165 (54), 152 (34), 77 (58), 43 (100), 41 (39); HRMS (EI-TOF) calcd for $C_{23}H_{29}N_3O$ (M^+) 363.2311, found 363.2320.

C. General Procedure for 9*H*-Fluorenes 2. To a solution of biaryl triazene **1** (1 mmol, 1.0 equiv) in toluene (5 mL) in a 25 mL round-bottom flask was added CF_3COOH (4.0 mmol, 4.0 equiv) dropwise at room temperature. And then the reaction mixture was heated to 100 °C and stirred for 1 h. On cooling to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (3 × 30 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.

*Ethyl 9H-fluorene-3-carboxylate (**2a**).* Prepared from biaryl triazene **1a** (337 mg, 1 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2a** (157 mg, 0.66 mmol, 66%) as a yellow solid: R_f = 0.57 (5:1 Petroleum ether/EtOAc); mp = 46−48 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 8.02 (dd, *J* = 7.8 Hz, 0.6 Hz, 1 H), 7.87 (d, *J* = 7.2 Hz, 1 H), 7.63−7.53 (m, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 3.96 (s, 2 H), 1.45 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.2, 143.2, 142.0, 140.9, 129.2, 128.1, 127.3, 127.0, 125.1, 124.8, 121.0, 120.3, 61.0, 37.1, 14.4; IR (ATR-FTIR) 1708, 1423, 1290, 1240, 746 cm^{-1}; MS (EI) *m/z* (%) 238 (M^+, 45), 213 (26), 193 (14), 183 (12), 165 (100), 163 (20); HRMS (EI-TOF) calcd for $C_{16}H_{14}O_2$ (M^+) 238.0994, found 238.0999.

*9H-Fluorene (**2b**).* Prepared from biaryl triazene **1b** (265 mg, 1 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2b** (150 mg, 0.9 mmol, 90%) as a white solid: R_f = 0.83 (5:1 Petroleum ether/EtOAc); mp = 107−108 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2 H), 7.58 (d, *J* = 7.2 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 2 H), 3.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.7, 126.69, 126.67, 125.0, 119.8, 36.9; IR (ATR-FTIR) 2922, 1444, 1305, 1236, 733 cm^{-1}; MS (EI) *m/z* (%) 166 (M^+, 100), 163 (16), 82 (13), 63 (12), 50 (10), 39 (11); HRMS (EI-TOF) calcd for $C_{13}H_{10}$ (M^+) 166.0783, found 166.0781.

*3-Methyl-9H-fluorene (**2c**).* Prepared from biaryl triazene **1c** (279 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2c** (153 mg, 0.85 mmol, 85%) as a yellow solid: R_f = 0.76 (10:1 Petroleum ether/EtOAc); mp = 64−66 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1 H), 7.63 (s, 1 H), 7.55 (d, *J* = 7.2 Hz, 1 H), 7.45 (d, *J* = 7.2 Hz, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.2 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 3.88 (s, 2 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.8, 141.7, 140.3, 136.3, 127.6, 126.6, 126.5, 125.0, 124.7, 120.4, 119.7, 36.5, 21.5; IR (ATR-FTIR) 2919, 1449, 1309, 809, 734 cm^{-1}; MS (EI) *m/z* (%) 180 (M^+, 100), 178 (31), 176 (13), 166

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(17), 165 (96), 89 (14); HRMS (EI-TOF) calcd for $C_{14}H_{12}$ (M^+) 180.0939, found 180.0937.

*3-Chloro-9H-fluorene (**2d**).* Prepared from biaryl triazene **1d** (299 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2d** (146 mg, 0.73 mmol, 73%) as a yellow solid: R_f = 0.69 (10:1 Petroleum ether/EtOAc); mp = 75−77 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.72 (m, 2 H), 7.55 (d, J = 7.2 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.40 (t, J = 7.2 Hz, 1 H), 7.34 (t, J = 7.4 Hz, 1 H), 7.30−7.26 (m, 1 H), 3.86 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.4, 141.3, 140.5, 132.7, 127.4, 126.9, 126.6, 126.0, 125.1, 120.1, 36.5; IR (ATR-FTIR) 1472, 1391, 1253, 809, 730 cm^{-1}; MS (EI) m/z (%) 200 (M^+, 20), 165 (100), 163 (29), 82 (10), 63 (7), 50 (6); HRMS (EI-TOF) calcd for $C_{13}H_9Cl$ (M^+) 200.0393, found 200.0395.

*3-Bromo-9H-fluorene (**2e**).* Prepared from biaryl triazene **1e** (343 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2e** (176 mg, 0.72 mmol, 72%) as a white solid: R_f = 0.68 (10:1 Petroleum ether/EtOAc); mp = 87−88 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1 H), 7.74 (d, J = 7.6 Hz, 1 H), 7.55 (d, J = 7.2 Hz, 1 H), 7.45−7.30 (m, 4 H), 3.84 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 143.5, 141.8, 140.4, 129.4, 127.4, 126.9, 126.4, 125.1, 123.0, 120.7, 120.1, 36.5; IR (ATR-FTIR) 1469, 1307, 1261, 803, 756 cm^{-1}; MS (EI) m/z (%) 246 (M^+, Br^{81}, 28), 244 (M^+, Br^{81}, 27), 165 (100), 163 (44), 82 (25), 63 (11), 50 (10); HRMS (EI-TOF) calcd for $C_{13}H_9Br$ (M^+) 243.9888, found 243.9889.

*9H-Fluorene-3-carbonitrile (**2f**).* Prepared from biaryl triazene **1f** (290 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2f** (100 mg, 0.52 mmol, 52%) as a yellow solid: R_f = 0.32 (10:1 Petroleum ether/EtOAc); mp = 85−87 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.79 (d, J = 7.2 Hz, 1 H), 7.65−7.54 (m, 3 H), 7.47−7.35 (m, 2 H), 3.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 142.9, 142.6, 139.6, 130.2, 128.1, 127.2, 125.7, 125.2, 123.3, 120.4, 119.4, 110.6, 37.2; IR (ATR-FTIR) 2226, 1450, 1392, 1303, 825, 764 cm^{-1}; MS (EI) m/z (%) 191 (M^+, 100), 190 (78), 163 (12), 81 (11), 63 (13), 50 (10), 39 (10); HRMS (EI-TOF) calcd for $C_{14}H_9N$ (M^+) 191.0735, found 191.0738.

*3-Fluoro-9H-fluorene (**2g**).* Prepared from biaryl triazene **1g** (283 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2g** (100 mg, 0.54 mmol, 54%) as a white solid: R_f = 0.73 (10:1 Petroleum ether/EtOAc); mp = 62−63 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 1 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.50−7.43 (m, 2 H), 7.40 (t, J = 7.2 Hz, 1 H), 7.35 (t, J = 7.2 Hz, 1 H), 7.01 (t, J = 8.2 Hz, 1 H), 3.86 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, $^1J_{C-F}$ = 241.2 Hz), 144.2, 143.6 (d, $^3J_{C-F}$ = 8.6 Hz), 140.9 (d, $^4J_{C-F}$ = 3.4 Hz), 138.4 (d, $^4J_{C-F}$ = 2.5 Hz), 127.3, 126.8, 125.8 (d, $^3J_{C-F}$ = 9.0 Hz), 125.1, 120.1, 113.5 (d, $^2J_{C-F}$ = 22.4 Hz), 106.8 (d, $^2J_{C-F}$ = 22.4 Hz), 36.3; IR (ATR-FTIR) 1482, 1448, 1305, 808, 724 cm^{-1}; MS (EI) m/z (%) 184 (M^+, 100), 183 (100), 163 (7), 157 (7), 92 (11), 81 (6); HRMS (EI-TOF) calcd for $C_{13}H_9F$ (M^+) 184.0688, found 184.0687.

*2-Fluoro-9H-fluorene (**2h**).* Prepared from biaryl triazene **1h** (284 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2h** (120 mg, 0.65 mmol, 65%) as a white solid: R_f = 0.70 (10:1 Petroleum ether/EtOAc); mp = 96−97 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.70 (m, 2 H), 7.57 (d, J = 7.2 Hz, 1 H), 7.42 (t, J = 7.2 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.28 (d, J = 7.6 Hz, 1 H), 7.12 (t, J = 8.8 Hz, 1 H), 3.91 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C-F}$ = 242.4 Hz), 145.2 (d, $^3J_{C-F}$ = 8.8 Hz), 142.9, 140.8, 137.7, 126.8, 126.3, 124.9, 120.6 (d, $^3J_{C-F}$ = 9.1 Hz), 119.5, 113.9 (d, $^2J_{C-F}$ = 23.3 Hz), 112.2 (d, $^2J_{C-F}$ = 22.8 Hz), 36.9 (d, $^4J_{C-F}$ = 2.0 Hz); IR (ATR-FTIR) 1482, 1305, 1175, 808, 763, 724 cm^{-1}; MS (EI) m/z (%) 184 (M^+, 100), 183 (95), 163 (7), 92 (12), 39 (7); HRMS (EI-TOF) calcd for $C_{13}H_9F$ (M^+) 184.0688, found 184.0685.

*2-Methoxy-9H-fluorene (**2i**).* Prepared from biaryl triazene **1i** (295 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2i** (153 mg, 0.78 mmol, 78%) as a light yellow solid: R_f = 0.62 (10:1 Petroleum ether/EtOAc); mp = 97−99 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.69 (m, 2 H), 7.54 (d, J = 7.6 Hz, 1 H), 7.39 (t, J = 7.2 Hz, 1 H), 7.29 (d, J = 6.8 Hz, 1 H), 7.14 (s, 1 H), 6.98 (d, J = 8.4 Hz, 1 H), 3.91 (s, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.0, 142.7, 141.6, 134.7, 126.7, 125.5, 124.8, 120.5, 119.0, 112.9, 110.5, 55.5, 37.0; IR (ATR-FTIR) 1606, 1457, 1265, 1218, 831, 764, 733 cm^{-1}; MS (EI) m/z (%) 196 (M^+, 100), 182 (11), 181 (64), 165 (15), 152 (77), 63 (10); HRMS (EI-TOF) calcd for $C_{14}H_{12}O$ (M^+) 196.0888, found 196.0886.

*1-Methyl-9H-fluorene (**2j**).* Prepared from biaryl triazene **1j** (279 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2j** (144 mg, 0.8 mmol, 80%) as a yellow solid: R_f = 0.80 (10:1 Petroleum ether/EtOAc); mp = 59−61 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 1 H), 7.68 (d, J = 7.6 Hz, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.42 (t, J = 7.4 Hz, 1 H), 7.38−7.31 (m, 2 H), 7.17 (d, J = 7.6 Hz, 1 H), 3.81 (s, 2 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.01, 142.00, 141.3, 134.2, 127.7, 127.0, 126.6, 126.5, 125.0, 120.0, 117.4, 35.8, 18.9; IR (ATR-FTIR) 1450, 1384, 1304, 751 cm^{-1}; MS (EI) m/z (%) 180 (M^+, 82), 178 (27), 165 (100), 152 (13), 76 (14), 39 (14); HRMS (EI-TOF) calcd for $C_{14}H_{12}$ (M^+) 180.0939, found 180.0941.

*Ethyl 8-methyl-9H-fluorene-3-carboxylate (**2k**).* Prepared from biaryl triazene **1k** (352 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2k** (166 mg, 0.66 mmol, 66%) as a yellow solid: R_f = 0.51 (10:1 Petroleum ether/EtOAc); mp = 76−78 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 8.01 (d, J = 8.0 Hz, 1 H), 7.71 (d, J = 7.6 Hz, 1 H), 7.60 (d, J = 8.0 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.16 (d, J = 7.6 Hz, 1 H), 4.44 (q, J = 7.1 Hz, 2 H), 3.81 (s, 2 H), 2.42 (s, 3 H), 1.45 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.1, 142.4, 142.0, 140.5, 134.3, 129.2, 128.3, 127.9, 127.3, 124.8, 121.1, 117.8, 61.0, 36.0, 18.8, 14.4; IR (ATR-FTIR) 1705, 1463, 1367, 1240, 1099, 794, 754 cm^{-1}; MS (EI) m/z (%) 252 (M^+, 93), 207 (10), 179 (100), 165 (16), 152 (28), 76 (7), 45 (7); HRMS (EI-TOF) calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1154.

*2-Methyl-9H-fluorene (**2l**).* Prepared from biaryl triazene **1l** (280 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2l** (144 mg, 0.80 mmol, 80%) as a yellow solid: R_f = 0.79 (10:1 Petroleum ether/EtOAc); mp = 70−72 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.53 (d, J = 7.2 Hz, 1 H), 7.39−7.33 (m, 2 H), 7.28 (d, J = 7.2 Hz, 1 H), 7.19 (d, J = 7.6 Hz, 1 H), 3.87 (s, 2 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.0, 141.8, 139.1, 136.5, 127.5, 126.6, 126.2, 125.7, 124.9, 119.6, 119.5, 36.7, 21.6; IR (ATR-FTIR) 1452, 1397, 1300, 822, 761, 730 cm^{-1}; MS (EI) m/z (%) 180 (M^+, 97), 178 (31), 165 (100), 152 (13), 89 (14); HRMS (EI-TOF) calcd for $C_{14}H_{12}$ (M^+) 180.0939, found 180.0936.

*Ethyl 7-methyl-9H-fluorene-3-carboxylate (**2m**).* Prepared from biaryl triazene **1m** (351 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2m** (161 mg, 0.64 mmol, 64%) as a yellow solid: R_f = 0.44 (10:1 Petroleum ether/EtOAc); mp = 54−56 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1 H), 7.98 (dd, J = 8.0 Hz, 1.6 Hz, 1 H), 7.75 (d, J = 7.6 Hz, 1 H), 7.56 (d, J = 7.6 Hz, 1 H), 7.36 (s, 1 H), 7.22 (d, J = 8.0 Hz, 1 H), 4.43 (q, J = 7.1 Hz, 2 H), 3.89 (s, 2 H), 2.44 (s, 3 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.1, 143.4, 142.1, 138.2, 137.2, 129.2, 127.8, 127.6, 125.7, 124.7, 120.6, 120.0, 60.9, 36.9, 21.6, 14.4; IR (ATR-FTIR) 1710, 1425, 1285, 1241,

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818, 754 cm^{-1}; MS (EI) *m/z* (%) 252 (M^+, 66), 223 (15), 207 (20), 179 (100), 178 (60), 152 (16); HRMS (EI-TOF) calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1155.

*Ethyl 6-methyl-9H-fluorene-3-carboxylate (**2n**).* Prepared from biaryl triazene **1n** (352 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2n** (180 mg, 0.71 mmol, 71%) as a yellow solid: R_f = 0.47 (10:1 Petroleum ether/EtOAc); mp = 56−57 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.2 Hz, 1 H), 8.00 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 7.69 (s, 1 H), 7.57 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.44 (d, *J* = 7.6 Hz, 1 H), 7.16 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 4.43 (q, *J* = 7.2 Hz, 2 H), 3.90 (s, 2 H), 2.47 (s, 3 H), 1.45 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.7, 142.1, 141.0, 140.3, 136.7, 129.2, 128.3, 128.0, 124.8, 124.7, 120.9, 60.9, 36.7, 21.5, 14.4; IR (ATR-FTIR) 1710, 1574, 1400, 1294, 1243, 1089, 763 cm^{-1}; MS (EI) *m/z* (%) 252 (M^+, 66), 223 (19), 207 (25), 179 (100), 178 (100), 165 (22), 152 (14), 96 (12), 76 (14), 45 (6); HRMS (EI-TOF) calcd for $C_{17}H_{16}O_2$ (M^+) 252.1150, found 252.1148.

*1-Chloro-9H-fluorene (**2o**).* Prepared from biaryl triazene **1o** (299 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2o** (138 mg, 0.69 mmol, 69%) as a white solid: R_f = 0.80 (10:1 Petroleum ether/EtOAc); mp = 65−66 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1 H), 7.68 (d, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 7.2 Hz, 1 H), 7.45−7.27 (m, 4 H), 3.91 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.6, 141.14, 141.11, 131.1, 128.4, 127.3, 126.9, 126.6, 125.1, 120.3, 118.2, 36.6; IR (ATR-FTIR) 1565, 1443, 749 cm^{-1}; MS (EI) *m/z* (%) 202 (M^+, Cl^{37}, 13), 200 (M^+, Cl^{35}, 38), 165 (100), 163 (48), 82 (13); HRMS (EI-TOF) calcd for $C_{13}H_9Cl$ (M^+) 200.0393, found 200.0395.

*1-Chloro-6-methyl-9H-fluorene (**2p**).* Prepared from biaryl triazene **1p** (313 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2p** (171 mg, 0.8 mmol, 80%) as a white solid: R_f = 0.74 (10:1 Petroleum ether/EtOAc); mp = 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 1 H), 7.58 (s, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.37−7.26 (m, 2 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 3.86 (s, 2 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.5, 141.2, 139.7, 136.6, 131.0, 128.33, 128.32, 126.5, 124.7, 120.9, 118.0, 36.2, 21.5; IR (ATR-FTIR) 1564, 1445, 1304, 1161, 786 cm^{-1}; MS (EI) *m/z* (%) 216 (M^+, Cl^{37}, 12), 214 (M^+, Cl^{35}, 36), 199 (16), 179 (100), 176 (16), 89 (11), 76 (10); HRMS (EI-TOF) calcd for $C_{14}H_{11}Cl$ (M^+) 214.0549, found 214.0554.

*Ethyl 8-chloro-9H-fluorene-3-carboxylate (**2q**).* Prepared from biaryl triazene **1q** (371 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2q** (160 mg, 0.59 mmol, 59%) as a white solid: R_f = 0.43 (10:1 Petroleum ether/EtOAc); mp = 93−95 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.71 (d, *J* = 7.2 Hz, 1 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.38−7.28 (m, 2 H), 4.43 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 2 H), 1.45 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.4, 142.6, 141.4, 141.1, 131.1, 129.5, 128.68, 128.66, 127.2, 124.9, 121.5, 118.6, 61.1, 36.7, 14.4; IR (ATR-FTIR) 1706, 1446, 1294, 1242, 788, 753, 695 cm^{-1}; MS (EI) *m/z* (%) 274 (M^+, Cl^{37}, 22), 272 (M^+, Cl^{35}, 48), 237 (31), 227 (36), 209 (20), 199 (100), 163 (55), 96 (23), 43 (30); HRMS (EI-TOF) calcd for $C_{16}H_{13}ClO_2$ (M^+) 272.0604, found 272.0604.

*Ethyl 8-bromo-9H-fluorene-3-carboxylate (**2r**).* Prepared from biaryl triazene **1r** (1.660 g, 4.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2r** (767 mg, 2.4 mmol, 61%) as a yellow solid: R_f = 0.54 (10:1 Petroleum ether/EtOAc); mp = 83−85 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.2 Hz, 1 H), 8.04 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 7.78 (d, *J* = 7.6 Hz, 1 H), 7.60 (dd, *J* = 8.0 Hz, 0.8 Hz, 1 H), 7.47 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 4.43 (q, *J* = 7.2 Hz, 2 H), 3.90 (s, 2 H), 1.45 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.3, 143.4, 142.5, 141.6, 130.2, 129.6, 128.9, 128.7, 124.9, 121.6, 120.2, 119.2, 61.1, 38.8, 14.4; IR (ATR-FTIR) 1701, 1601, 1413, 1245, 1102, 749, 639 cm^{-1}; MS (EI) *m/z* (%) 318 (M^+, Br^{81}, 21), 316 (M^+, Br^{79}, 21), 243 (66), 237 (50), 209 (20), 163 (100), 152 (23), 137 (12), 82 (14), 45 (16); HRMS (EI-TOF) calcd for $C_{16}H_{13}BrO_2$ (M^+) 316.0099, found 316.0106.

*2-Chloro-9H-fluorene (**2s**).* Prepared from biaryl triazene **1s** (300 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2s** (150 mg, 0.75 mmol, 75%) as a yellow solid: R_f = 0.75 (10:1 Petroleum ether/EtOAc); mp = 78−79 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.58−7.47 (m, 2 H), 7.46−7.28 (m, 3 H), 3.89 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 142.9, 140.6, 140.2, 132.3, 127.02, 126.97, 126.92, 125.3, 125.1, 120.7, 119.9, 36.7; IR (ATR-FTIR) 1470, 1445, 1298, 870, 821, 761 cm^{-1}; MS (EI) *m/z* (%) 202 (M^+, Cl^{37}, 19), 200 (M^+, Cl^{35}, 52), 165 (100), 163 (36), 82 (19), 63 (11); HRMS (EI-TOF) calcd for $C_{13}H_9Cl$ (M^+) 200.0393, found 200.0395.

*Ethyl 7-chloro-9H-fluorene-3-carboxylate (**2t**).* Prepared from biaryl triazene **1t** (371 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2t** (161 mg, 0.59 mmol, 59%) as a white solid: R_f = 0.45 (10:1 Petroleum ether/EtOAc); mp = 103−104 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 7.73 (d, *J* = 8.4 Hz, 1 H), 7.55 (d, *J* = 7.6 Hz, 1 H), 7.50 (s, 1 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 3.88 (s, 2 H), 1.44 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 147.8, 144.7, 140.9, 139.4, 133.0, 129.4, 128.3, 127.3, 125.3, 124.8, 121.1, 121.0, 61.0, 36.9, 14.3; IR (ATR-FTIR) 1702, 1423, 1308, 1244, 823, 754 cm^{-1}; MS (EI) *m/z* (%) 274 (M^+, Cl^{37}, 30), 272 (M^+, Cl^{35}, 78), 237 (27), 227 (30), 209 (22), 199 (100), 163 (64), 96 (13), 82 (13), 43 (8); HRMS (EI-TOF) calcd for $C_{16}H_{13}ClO_2$ (M^+) 272.0604, found 272.0602.

*Ethyl 6-chloro-9H-fluorene-3-carboxylate (**2u**).* Prepared from biaryl triazene **1u** (371 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2u** (164 mg, 0.60 mmol, 60%) as a white solid: R_f = 0.48 (10:1 Petroleum ether/EtOAc); mp = 78−79 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 8.02 (d, *J* = 8.4 Hz, 1 H), 7.78 (s, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 3.86 (s, 2 H), 1.44 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.5, 142.6, 141.3, 140.8, 133.1, 129.5, 128.7, 127.2, 126.0, 124.9, 121.2, 120.5, 61.1, 36.6, 14.4; IR (ATR-FTIR) 1695, 1434, 1392, 1245, 1100, 810, 754 cm^{-1}; MS (EI) *m/z* (%) 274 (M^+, Cl^{37}, 15), 272 (M^+, Cl^{35}, 46), 237 (25), 267 (19), 199 (100), 163 (64), 96 (14), 82 (15), 45 (8); HRMS (EI-TOF) calcd for $C_{16}H_{13}ClO_2$ (M^+) 272.0604, found 272.0608.

*Methyl 9H-fluorene-3-carboxylate (**2v**).* Prepared from biaryl triazene **1v** (323 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2v** (173 mg, 0.77 mmol, 77%) as a white solid: R_f = 0.56 (10:1 Petroleum ether/EtOAc); mp = 71−73 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1 H), 8.00 (dd, *J* = 8.0 Hz, 1.2 Hz, 1 H), 7.85 (d, *J* = 7.6 Hz, 1 H), 7.64−7.50 (m, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 3.97 (s, 3 H), 3.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 148.3, 143.1, 142.0, 140.8, 128.9, 128.1, 127.3, 127.0, 125.1, 124.8, 121.0, 120.3, 52.1, 37.0; IR (ATR-FTIR) 1714, 1430, 1293, 1243, 1095, 749 cm^{-1}; MS (EI) *m/z* (%) 224 (M^+, 58), 209 (10), 193 (14), 165 (100), 163 (32), 82 (13), 39 (5); HRMS (EI-TOF) calcd for $C_{15}H_{12}O_2$ (M^+) 224.0837, found 224.0836.

*3-Ethyl 6-methyl 9H-fluorene-3,6-dicarboxylate (**2w**).* Prepared from biaryl triazene **1w** (395 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2w** (151 mg, 0.51 mmol, 51%) as a light yellow solid: R_f = 0.15 (10:1 Petroleum ether/EtOAc); mp = 94−96 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 2 H), 8.09−7.94 (m, 2 H), 7.63−7.51

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(m, 2 H), 4.43 (q, J = 7.2 Hz, 2 H), 3.97 (s, 3 H), 3.94 (s, 2 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.7, 148.1, 148.0, 141.2, 141.1, 129.5, 129.1, 128.7, 128.6, 124.9, 124.8, 121.4, 121.3, 61.0, 52.2, 37.2, 14.4; IR (ATR-FTIR) 1708, 1437, 1364, 1258, 1103, 749 cm^{-1}; MS (EI) m/z (%) 296 (M^+, 57), 251 (33), 237 (35), 223 (100), 209 (24), 192 (15), 163 (57), 82 (22), 43 (16); HRMS (EI-TOF) calcd for $C_{18}H_{16}O_4$ (M^+) 296.1049, found 296.1050.

*3-(tert-Butyl)-9H-fluorene-1-carbaldehyde (**2x**).* Prepared from biaryl triazene **1x** (349 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2x** (138 mg, 0.55 mmol, 55%) as a light yellow solid: R_f = 0.54 (10:1 Petroleum ether/EtOAc); mp = 127−128 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1 H), 8.08 (s, 1 H), 7.86 (d, J = 7.2 Hz, 1 H), 7.82 (s, 1 H), 7.60 (d, J = 7.6 Hz, 1 H), 7.41 (t, J = 7.4 Hz, 1 H), 7.36 (t, J = 7.2 Hz, 1 H), 4.20 (s, 2 H), 1.47 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 151.0, 144.0, 143.3, 141.5, 140.1, 132.2, 127.8, 127.3, 126.7, 125.1, 122.2, 119.8, 36.6, 34.9, 31.5; IR (ATR-FTIR) 2953, 1689, 1481, 1388, 1257, 1122, 756, 725 cm^{-1}; MS (EI) m/z (%) 250 (M^+, 100), 235 (100), 207 (10), 191 (30), 189 (39), 178 (58), 165 (78), 163 (22), 152 (17), 57 (17), 41 (14); HRMS (EI-TOF) calcd for $C_{18}H_{18}O$ (M^+) 250.1358, found 250.1360.

*Ethyl 6-(tert-butyl)-8-formyl-9H-fluorene-3-carboxylate (**2y**).* Prepared from biaryl triazene **1y** (421 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2y** (148 mg, 0.46 mmol, 46%) as a light yellow solid: R_f = 0.26 (10:1 Petroleum ether/EtOAc); mp = 157−159 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1 H), 8.48 (s, 1 H), 8.14 (s, 1 H), 8.04 (d, J = 7.6 Hz, 1 H), 7.84 (s, 1 H), 7.63 (d, J = 8.0 Hz, 1 H), 4.44 (q, J = 7.1 Hz, 2 H), 4.23 (s, 2 H), 1.50−1.44 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 166.8, 151.5, 149.1, 142.4, 141.2, 140.5, 132.2, 129.3, 128.69, 128.66, 125.0, 122.6, 121.0, 61.1, 36.9, 35.0, 31.5, 14.4; IR (ATR-FTIR) 2928, 1691, 1461, 1385, 1239, 1114, 751 cm^{-1}; MS (EI) m/z (%) 322 (M^+, 100), 307 (85), 277 (21), 249 (18), 234 (25), 202 (17), 191 (24), 189 (34), 165 (44), 57 (28), 41 (23); HRMS (EI-TOF) calcd for $C_{21}H_{22}O_3$ (M^+) 322.1569, found 322.1569.

*1-(3-(tert-Butyl)-9H-fluoren-1-yl)ethanone (**2z**).* Prepared from biaryl triazene **1z** (363 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2z** (161 mg, 0.61 mmol, 61%) as a white solid: R_f = 0.45 (10:1 Petroleum ether/EtOAc); mp = 92−94 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1 H), 7.90 (s, 1 H), 7.84 (d, J = 7.6 Hz, 1 H), 7.60 (d, J = 7.2 Hz, 1 H), 7.39 (t, J = 7.2 Hz, 1 H), 7.34 (t, J = 7.4 Hz, 1 H), 4.22 (s, 2 H), 2.71 (s, 3 H), 1.46 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 150.5, 144.5, 143.2, 141.3, 140.4, 133.4, 127.2, 126.6, 125.3, 125.0, 121.1, 119.7, 38.6, 34.9, 31.6, 28.2; IR (ATR-FTIR) 2957, 1683, 1458, 1357, 1240, 765 cm^{-1}; MS (EI) m/z (%) 264 (M^+, 61), 249 (43), 189 (19), 178 (21), 165 (41), 57 (22), 43 (100), 41 (19); HRMS (EI-TOF) calcd for $C_{19}H_{20}O$ (M^+) 264.1514, found 264.1520.

*1,3-Dimethyl-9H-fluorene (**2aa**).* Prepared from biaryl triazene **1aa** (293 mg, 1.0 mmol) according to the general procedure **C**. Purification via flash column chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2aa** (179 mg, 0.92 mmol, 92%) as a white solid: R_f = 0.81 (10:1 Petroleum ether/EtOAc); mp = 78−80 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.2 Hz, 1 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.47 (s, 1 H), 7.38 (dt, J = 7.2 Hz, 0.4 Hz, 1 H), 7.30 (dt, J = 7.4 Hz, 1.2 Hz, 1 H), 6.98 (s, 1 H), 3.76 (s, 2 H), 2.45 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.1, 141.5, 139.1, 136.7, 133.8, 128.8, 126.6, 126.4, 125.0, 119.9, 118.0, 35.5, 21.4, 18.8; IR (ATR-FTIR) 2921, 1609, 1449, 1021, 762, 728 cm^{-1}; MS (EI) m/z (%) 194 (M^+, 56), 179 (100), 165 (17), 152 (15), 139 (10), 89 (11), 63 (7), 39 (15); HRMS (EI-TOF) calcd for $C_{15}H_{14}$ (M^+) 194.1096, found 194.1089.

D. Experiment of Investigation of the Reaction Mechanism.

*D1. Procedure for Compounds of **1c-d_3** and **1a-d_3**.* **1c-d_3**. In a 50 mL Schlenck tube, 1-iodo-2-methyl-D_3-benzene (660 mg, 3.0 mmol, 1.0 equiv), (*E*)-5-methyl-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid (839 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (104 mg, 0.09 mmol, 0.03 equiv) and Cs_2CO_3 (2.444 g, 7.5 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 18 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. On cooling to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1c-d_3** (666 mg, 2.4 mmol, 80%) as brown oil: R_f = 0.72 (5:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 1 H), 7.22−7.17 (m, 4 H), 7.13 (d, J = 7.6 Hz, 1 H), 7.01 (s, 1 H), 3.53 (br, 4 H), 2.36 (s, 3 H), 1.92−1.84 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.9, 136.4, 134.3, 131.0, 130.3, 130.0, 128.9, 128.4, 126.4, 124.8, 116.7, 23.7, 21.0, 19.5 (m); IR (ATR-FTIR) 1600, 1420, 1321, 1107, 819, 756, 695 cm^{-1}; MS (EI) m/z (%) 282 (M^+, 43), 212 (24), 198 (21), 184 (61), 168 (100), 154 (11), 117 (6), 70 (7), 41 (24); HRMS (EI-TOF) calcd for $C_{18}H_{18}D_3N_3$ (M^+) 282.1924, found 282.1929.

1a-d_3. In a 50 mL Schlenck tube, 1-iodo-2-methyl-D_3-benzene (442 mg, 2.0 mmol, 1.0 equiv), (*E*)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid (698 mg, 2.4 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.03 equiv) and Cs_2CO_3 (1.629 g, 5.0 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 12 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. On cooling to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **1a-d_3** (612 mg, 1.8 mmol, 90%) as a yellow solid: R_f = 0.57 (5:1 Petroleum ether/EtOAc); mp = 89−90 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.6 Hz, 1.8 Hz, 1 H), 7.90 (d, J = 2.4 Hz, 1 H), 7.51 (d, J = 8.4 Hz, 1 H), 7.25−7.12 (m, 4 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.87 (br, 2 H), 3.29 (br, 2 H), 1.92 (br, 4 H), 1.38 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 152.3, 140.0, 136.5, 136.3, 132.1, 130.0, 129.4, 129.1, 126.9, 126.4, 125.0, 116.5, 60.6, 50.8, 46.4, 23.8, 23.4, 19.5 (m), 14.3; IR (ATR-FTIR) 1694, 1597, 1395, 1234, 1108, 771, 694 cm^{-1}; MS (EI) m/z (%) 340 (M^+, 21), 270 (12), 196 (14), 183 (16), 170 (100), 168 (100), 154 (18), 70 (11), 41 (17); HRMS (EI-TOF) calcd for $C_{20}H_{20}D_3N_3O_2$ (M^+) 340.1979, found 340.1973.

*D2. Procedure for Compounds of **2c-d_2** and **2a-d_2**. 9,9-Dideuterium-3-methyl-9H-fluorene (**2c-d_2**).* In a 25 mL round-bottom, the solution of **1c-d_3** (281 mg, 1.0 mmol, 1.0 equiv) in toluene (5 mL) flask was stirred at room temperature, and then CF_3COOH (456 mg, 4.0 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (3 × 50 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2c-d_2** (152 mg, 0.84 mmol, 84%) as a white solid: R_f = 0.76 (10:1 Petroleum ether/EtOAc); mp = 67−69 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 1 H), 7.63 (s, 1 H), 7.55 (d, J = 7.6 Hz, 1 H), 7.44 (d, J = 7.6 Hz, 1 H), 7.38 (t, J = 8.0 Hz, 1 H), 7.30 (t, J = 7.8 Hz, 1 H), 7.14 (d, J = 7.6 Hz, 1 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 141.9, 141.8, 140.2, 136.3, 127.6, 126.6, 126.5, 125.0, 124.7, 120.4, 119.7, 35.9 (m), 21.5; IR (ATR-FTIR) 1611, 1447, 1289, 1190, 754 cm^{-1}; MS (EI) m/z (%) 182 (M^+, 82), 179 (13), 167 (100), 153 (10), 90 (8), 77 (5), 39 (4); HRMS (EI-TOF) calcd for $C_{14}H_{10}D_2$ (M^+) 182.1065, found 182.1068.

*9,9-Dideuterium-ethyl 9H-fluorene-3-carboxylate (**2a-d_2**).* In a 25 mL round-bottom, the solution of **1a-d_3** (273 mg, 0.80 mmol, 1.0 equiv) in toluene (4 mL) flask was stirred at room temperature, and

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then CF_3COOH (365 mg, 3.2 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (3 × 50 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **2a-*d*$_2$** (122 mg, 0.51 mmol, 63%) as a white solid: R_f = 0.54 (10:1 Petroleum ether/EtOAc); mp = 47−48 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 0.8 Hz, 1 H), 8.01 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.87 (d, J = 7.2 Hz, 1 H), 7.64−7.52 (m, 2 H), 7.41 (dt, J = 7.4 Hz, 1.1 Hz, 1 H), 7.34 (dt, J = 7.3 Hz, 1.1 Hz, 1 H), 4.43 (q, J = 7.2 Hz, 2 H), 1.45 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.1, 143.0, 142.1, 140.9, 129.3, 128.0, 127.2, 127.0, 125.0, 124.8, 120.9, 120.2, 61.0, 36.4 (m), 14.4; IR (ATR-FTIR) 1708, 1612, 1450, 1240, 1100, 741 cm^{-1}; MS (EI) m/z (%) 240 (M$^+$, 53), 211 (13), 195 (50), 167 (100), 141 (7), 97 (9), 83 (14), 43 (5); HRMS (EI-TOF) calcd for $C_{16}H_{12}D_2O_2$ (M$^+$) 240.1119, found 240.1119.

D3. Procedure for Compound 3-Bromo-2-methylbiphenyl. In a 50 mL Schlenck tube, 1-bromo-3-iodo-2-methylbenzene (6.0 mmol, 1.0 equiv), phenylboronic acid (6.3 mmol, 1.05 equiv), $Pd(PPh_3)_4$ (0.18 mmol, 0.03 equiv) and Cs_2CO_3 (15 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 24 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reation mixture was cooled to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography yielding 3-bromo-2-methyl-1,1′-biphenyl (1.236 g, 5.0 mmol, 83%) as yellow oil.

*D4. Procedure for Compounds of **3a** and **3b**. (E)-1-((2′,5-Dimethyl-[1,1′:3′,1″-terphenyl]-2-yl)diazenyl)pyrrolidine (**3a**).* In a 50 mL Schlenck tube, 3-bromo-2-methyl-1,1′-biphenyl (738 mg, 3.0 mmol, 1.0 equiv), (*E*)-5-methyl-2-(pyrrolidin-1-yldiazenyl)-phenylboronic acid (839 mg, 3.6 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (104 mg, 0.09 mmol, 0.03 equiv) and Cs_2CO_3 (2.444 g, 7.5 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 18 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **3a** (1.034 g, 2.9 mmol, 97%) as a purple solid: R_f = 0.57 (10:1 Petroleum ether/EtOAc); mp = 111−113 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.30 (m, 6 H), 7.25−7.16 (m, 3 H), 7.14 (d, J = 8.4 Hz, 1 H), 7.09 (s, 1 H), 3.58 (br, 4 H), 2.38 (s, 3 H), 2.01 (s, 3 H), 1.94−1.86 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 142.9, 141.7, 141.6, 136.8, 134.5, 134.1, 131.0, 129.3, 129.1, 128.5, 128.2, 127.9, 126.5, 124.6, 116.7, 23.7, 21.0, 18.5; IR (ATR-FTIR) 1578, 1414, 1311, 1107, 809, 760, 700 cm^{-1}; MS (EI) m/z (%) 355 (M$^+$, 5), 285 (10), 270 (44), 257 (64), 242 (100), 215 (39), 179 (28), 165 (56), 115 (18), 91 (24), 77 (16), 41 (29); HRMS (EI-TOF) calcd for $C_{24}H_{25}N_3$ (M$^+$) 355.2048, found 355.2052.

*(E)-Ethyl 2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′:3′,1″-terphenyl]-3-carboxylate (**3b**).* In a 50 mL Schlenck tube, 3-bromo-2-methyl-1,1′-biphenyl (**S5**) (493 mg, 2.0 mmol, 1.0 equiv), (E)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid (699 mg, 2.4 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.03 equiv) and Cs_2CO_3 (1.629 g, 5.0 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 12 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **3b** (831 mg, 2.0 mmol, 99%) as a yellow solid: R_f = 0.32 (10:1 Petroleum ether/EtOAc); mp = 144−146 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.94 (m, 2 H), 7.52 (d, J = 8.4 Hz, 1 H), 7.43−7.36 (m, 2 H), 7.35−7.28 (m, 3 H), 7.25−7.22 (m, 1 H), 7.21−7.14 (m, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 3.86 (br, 2 H), 3.36 (br, 2 H), 2.01−1.88 (m, 7 H), 1.37 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 152.3, 142.7, 141.7, 140.8, 136.7, 134.1, 132.1, 129.4, 129.3, 129.1, 128.6, 128.0, 126.6, 126.4, 124.7, 116.5, 60.7, 50.9, 46.3, 23.8, 23.4, 18.4, 14.4; IR (ATR-FTIR) 1698, 1597, 1399, 1229, 1103, 732, 697 cm^{-1}; MS (EI) m/z (%) 413 (M$^+$, 7), 328 (61), 315 (56), 241 (100), 226 (31), 202 (29), 165 (46), 115 (16), 91 (19), 70 (34), 41 (52); HRMS (EI-TOF) calcd for $C_{26}H_{27}N_3O_2$ (M$^+$) 413.2103, found 413.2116.

*D5. Procedure for Compounds of **4a** and **4b**. 6-Methyl-1-phenyl-9H-fluorene (**4a**).* In a 25 mL round-bottom flask, the solution of (*E*)-1-((2′,5-dimethyl-[1,1′:3′,1″-terphenyl]-2-yl)diazenyl)pyrrolidine (**3a**) (375 mg, 1.06 mmol, 1.0 equiv) in toluene (5 mL) was stirred at room temperature, and then CF_3COOH (483 mg, 4.24 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (5 × 30 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **4a** (200 mg, 0.78 mmol, 74%) as a yellow solid: R_f = 0.82 (10:1 Petroleum ether/EtOAc); mp = 72−74 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.2 Hz, 1 H), 7.67 (s, 1 H), 7.62−7.56 (m, 2 H), 7.54−7.46 (m, 3 H), 7.45−7.39 (m, 2 H), 7.34 (d, J = 7.2 Hz, 1 H), 7.15 (d, J = 7.6 Hz, 1 H), 3.94 (s, 2 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 141.7, 141.3, 141.1, 140.4, 139.1, 136.3, 128.53, 128.45, 127.8, 127.4, 127.2, 124.5, 120.5, 118.8, 36.5, 21.6; IR (ATR-FTIR) 1594, 1455, 1159, 799, 757, 696 cm^{-1}; MS (EI) m/z (%) 256 (M$^+$, 100), 241 (56), 226 (9), 178 (9), 165 (8), 120 (13), 77 (11), 51 (7), 39 (7); HRMS (EI-TOF) calcd for $C_{20}H_{16}$ (M$^+$) 256.1252, found 256.1260.

*Ethyl 8-phenyl-9H-fluorene-3-carboxylate (**4b**).* In a 25 mL round-bottom flask, the solution of (*E*)-ethyl 2′-methyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′:3′,1″-terphenyl]-3-carboxylate (**3b**) (333 mg, 0.81 mmol, 1.0 equiv) in toluene (4 mL) was stirred at room temperature, and then CF_3COOH (368 mg, 3.24 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (5 × 30 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **4b** (184 mg, 0.59 mmol, 73%) as a white solid: R_f = 0.41 (10:1 Petroleum ether/EtOAc); mp = 89−91 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1 H), 8.02 (dd, J = 7.8 Hz, 1.4 Hz, 1 H), 7.88 (d, J = 7.6 Hz, 1 H), 7.58−7.46 (m, 6 H), 7.44−7.35 (m, 2 H), 4.45 (q, J = 7.2 Hz, 2 H), 4.00 (s, 2 H), 1.47 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.2, 141.9, 141.3, 140.9, 140.8, 139.2, 129.3, 128.5, 128.4, 128.2, 127.9, 127.7, 127.3, 124.6, 121.1, 119.3, 61.0, 37.0, 14.4; IR (ATR-FTIR) 1708, 1453, 1242, 1111, 753, 700 cm^{-1}; MS (EI) m/z (%) 314 (M$^+$, 100), 285 (24), 269 (43), 241 (100), 226 (12), 215 (9), 163 (9), 77 (6), 45 (7); HRMS (EI-TOF) calcd for $C_{22}H_{18}O_2$ (M$^+$) 314.1307, found 314.1303.

In order to confirm the structure of **4b**, the Suzuki−Miyaura cross-coupling reaction between ethyl 8-bromo-9*H*-fluorene-3-carboxylate (**2r**) and phenyl boronic acid was carried out.

*Ethyl 8-phenyl-9H-fluorene-3-carboxylate (**4b**).* In a 25 mL Schlenck tube, ethyl 8-bromo-9H-fluorene-3-carboxylate (**2r**) (316 mg, 1.0 mmol, 1.0 equiv), phenylboronic acid (147 mg, 1.2 mmol, 1.2

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equiv), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 0.03 equiv) and Cs_2CO_3 (815 mg, 2.5 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 6 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to ambient temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **4b** (198 mg, 0.63 mmol, 63%) as a white solid.

E. Synthesis of Unsymmetrical Functionalized 6,12-Dihydroindeno[1,2-*b*]fluorines 11a–c. *E1. Procedure for Compounds of **10a–c**.* A dry and nitrogen-flushed 100 mL Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of 1,4-dibromo-2,5-dimethylbenzene (10 mmol, 1.0 equiv) in dry THF (20 mL). *n*-BuLi (11 mmol, 1.6 M in THF, 1.1 equiv) was then added dropwise at −78 °C. After the reaction mixture was continuously stirred at −78 °C for 3 h, a complete Br/Li exchange was observed as indicated by thin layer chromatography (TLC). $ZnBr_2$ (12 mmol, 1.0 M in THF, 1.2 equiv) was added at −78 °C. The reaction mixture was slowly warmed to room temperature for 0.5 h, and stirring was continued for further 10 min when it was brought to room temperature. $Pd(PPh_3)_4$ (0.3 mmol, 0.03 equiv) and **6** (9 mmol, 0.9 equiv) were added. The reaction mixture was stirred at 50 °C for 12 h before quenched by saturated aqueous NH_4Cl (20 mL). The resulting mixture was extracted with ethyl acetate (3 × 30 mL), and the combined organic fractions were dried (Na_2SO_4) and concentrated in vacuo. Purification by flash chromatography yielded the pure product **7**.

In a 50 mL round-bottom flask, the solution of **7** (1.0 mmol, 1.0 equiv) in toluene (5 mL) was stirred at room temperature, and then CF_3COOH (4.0 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The resulting reaction mixture was extracted with ethyl acetate (3 × 30 mL) and washed with water (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography gave the pure product **8**.

*(E)-Ethyl 3-(3-methyl-9H-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)-benzoate (**10a**).* In a 50 mL Schlenck tube, 2-bromo-3-methyl-9H-fluorene (**8a**) (516 mg, 2.0 mmol, 1.0 equiv), (E)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid **9** (699 mg, 2.4 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.03 equiv) and Cs_2CO_3 (1.629 g, 5 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 12 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to ambient temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **10a** (723 mg, 1.7 mmol, 85%) as a yellow solid: R_f = 0.29 (10:1 Petroleum ether/EtOAc); mp = 159–161 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1 H), 7.99 (s, 1 H), 7.81 (d, J = 7.6 Hz, 1 H), 7.65 (s, 1 H), 7.60–7.53 (m, 2 H), 7.44–7.35 (m, 2 H), 7.30 (t, J = 7.2 Hz, 1 H), 4.39 (q, J = 7.1 Hz, 2 H), 4.02–3.67 (m, 4 H), 3.29 (br, 2 H), 2.23 (s, 3 H), 1.90 (br, 4 H), 1.40 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.4, 143.7, 141.8, 140.5, 140.1, 138.8, 136.8, 135.3, 132.2, 129.4, 126.6, 126.40, 126.36, 126.28, 125.0, 120.4, 119.6, 116.4, 60.7, 50.9, 46.4, 36.5, 23.8, 23.3, 20.6, 14.3; IR (ATR-FTIR) 1707, 1599, 1401, 1235, 1100, 774, 744 cm^{-1}; MS (EI) m/z (%) 425 (M^+, 3), 340 (39), 327 (11), 298 (7), 254 (100), 239 (26), 226 (8), 126 (14), 70 (7), 41 (8); HRMS (EI-TOF) calcd for $C_{27}H_{27}N_3O_2$ (M^+) 425.2103, found 425.2099.

*(E)-Ethyl 3-(6-fluoro-3-methyl-9H-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)benzoate (**10b**).* In a 50 mL Schlenck tube, 2-bromo-6-fluoro-3-methyl-9H-fluorene (**8b**) (1.017 g, 3.68 mmol, 1.0 equiv), (E)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid **9** (1.287 g, 4.42 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (128 mg, 0.11 mmol, 0.03 equiv) and Cs_2CO_3 (2.998 g, 9.2 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 24 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to ambient temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **10b** (1.388 g, 3.1 mmol, 85%) as a brown solid: R_f = 0.27 (10:1 Petroleum ether/EtOAc); mp = 160–162 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.4 Hz, 1.6 Hz, 1 H), 7.95 (d, J = 1.6 Hz, 1 H), 7.61–7.53 (m, 2 H), 7.49–7.41 (m, 2 H), 7.38 (s, 1 H), 6.98 (dt, J = 8.8 Hz, 2.4 Hz, 1 H), 4.37 (q, J = 7.2 Hz, 2 H), 3.88 (br, 2 H), 3.84 (s, 2 H), 3.29 (br, 2 H), 2.21 (s, 3 H), 1.90 (br, 4 H), 1.39 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 162.6 (d, $^1J_{C-F}$ = 240.5 Hz), 152.4, 143.8 (d, $^3J_{C-F}$ = 8.9 Hz), 141.1, 139.8 (d, $^4J_{C-F}$ = 2.6 Hz), 139.6, 138.9 (d, $^4J_{C-F}$ = 2.2 Hz), 136.6, 135.6, 132.1, 130.5, 129.5, 126.4, 125.8 (d, $^3J_{C-F}$ = 9.1 Hz), 120.6, 120.0, 116.4, 113.0 (d, $^2J_{C-F}$ = 22.2 Hz), 106.6 (d, $^2J_{C-F}$ = 22.4 Hz), 60.7, 50.9, 46.4, 35.9, 23.8, 23.3, 20.6, 14.4; IR (ATR-FTIR) 1705, 1409, 1295, 1247, 1088, 756 cm^{-1}; MS (EI) m/z (%) 443 (M^+, 10), 358 (31), 346 (45), 303 (9), 272 (100), 257 (35), 183 (21), 135 (9), 70 (7), 43 (5); HRMS (EI-TOF) calcd for $C_{27}H_{26}FN_3O_2$ (M^+) 443.2009, found 443.2014.

*(E)-Ethyl 3-(3-methyl-6-(trifluoromethyl)-9H-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)benzoate (**10c**).* In a 50 mL Schlenck tube, 2-bromo-3-methyl-6-(trifluoromethyl)-9H-fluorene (**8c**) (652 mg, 2.0 mmol, 1.0 equiv), (E)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)-phenylboronic acid **9** (699 mg, 2.4 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 0.03 equiv) and Cs_2CO_3 (1.629 g, 5 mmol, 2.5 equiv) were dissolved in dioxane/H_2O (5/1, v:v, 12 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to ambient temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **10c** (740 mg, 1.5 mmol, 75%) as a yellow solid: R_f = 0.21 (10:1 Petroleum ether/EtOAc); mp = 182–184 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.99 (m, 2 H), 7.95 (d, J = 1.2 Hz, 1 H), 7.68 (s, 1 H), 7.63 (d, J = 7.6 Hz, 1 H), 7.58–7.52 (m, 2 H), 7.41 (s, 1 H), 4.37 (q, J = 7.2 Hz, 2 H), 4.04–3.73 (m, 4 H), 3.28 (br, 2 H), 2.21 (s, 3 H), 1.91 (br, 4 H), 1.39 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 152.4, 147.3, 142.5, 140.2, 140.0, 139.3, 136.5, 135.9, 132.1, 129.6, 129.2 (q, $^2J_{C-F}$ = 30.8 Hz), 126.5, 125.2, 123.0 (q, $^3J_{C-F}$ = 3.8 Hz), 120.8, 116.5, 116.4, 60.8, 51.0, 46.6, 23.9, 23.3, 20.6, 14.4; IR (ATR-FTIR) 1700, 1599, 1398, 1235, 1107, 874, 824, 775 cm^{-1}; MS (EI) m/z (%) 493 (M^+, 5), 408 (21), 395 (21), 349 (10), 322 (100), 252 (66), 239 (8), 126 (16), 70 (11), 41 (11); HRMS (EI-TOF) calcd for $C_{28}H_{26}F_3N_3O_2$ (M^+) 493.1977, found 493.1976.

*E2. Procedure for Compounds of **11a–c**. Ethyl 6,12-dihydroindeno[1,2-b]fluorene-3-carboxylate (**11a**).* In a 25 mL round-bottom flask, the solution of (*E*)-ethyl 3-(3-methyl-9*H*-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)benzoate (**10a**) (250 mg, 0.59 mmol, 1.0 equiv) in toluene (5 mL) was stirred at room temperature, and then CF_3COOH (269 mg, 2.36 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The resulting reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **11a** (87 mg, 0.27 mmol, 45%) as a white solid: R_f = 0.42 (10:1 Petroleum ether/EtOAc); mp = 183–185 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400

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MHz, $CDCl_3$) δ 8.43 (s, 1 H), 7.99 (d, J = 7.6 Hz, 1 H), 7.96 (s, 1 H), 7.87 (s, 1 H), 7.78 (d, J = 7.6 Hz, 1 H), 7.58−7.52 (m, 2 H), 7.39 (t, J = 7.4 Hz, 1 H), 7.31 (t, J = 7.2 Hz, 1 H), 4.44 (q, J = 7.1 Hz, 2 H), 3.93 (s, 4 H), 1.46 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.6, 143.7, 142.4, 142.2, 142.1, 141.5, 141.3, 139.8, 129.2, 127.7, 126.7, 126.6, 125.0, 124.7, 120.6, 119.6, 116.7, 116.3, 60.9, 36.8, 36.6, 14.4; IR (ATR-FTIR) 1705, 1409, 1295, 1247, 1088, 756 cm^{-1}; MS (EI) m/z (%) 326 (M^+, 92), 298 (12), 281 (13), 253 (100), 200 (6), 149 (10), 140 (25), 45 (34); HRMS (EI-TOF) calcd for $C_{23}H_{18}O_2$ (M^+) 326.1307, found 326.1306.

*Ethyl 9-fluoro-6,12-dihydroindeno[1,2-b]fluorene-3-carboxylate (**11b**).* In a 25 mL round-bottom flask, the solution of (*E*)-ethyl 3-(6-fluoro-3-methyl-9*H*-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)-benzoate (**10b**) (222 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL) was stirred at room temperature, and then CF_3COOH (228 mg, 2.0 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The resulting reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **11b** (35 mg, 0.1 mmol, 20%) as a yellow solid: R_f = 0.38 (10:1 Petroleum ether/EtOAc); mp = 147−149 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1 H), 7.98 (d, J = 8.0 Hz, 1 H), 7.92 (s, 1 H), 7.79 (s, 1 H), 7.54 (d, J = 7.6 Hz, 1 H), 7.47−7.37 (m, 2 H), 6.98 (t, J = 8.6 Hz, 1 H), 4.43 (q, J = 7.2 Hz, 2 H), 3.92 (s, 2 H), 3.85 (s, 2 H), 1.46 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.6 (d, $^1J_{C-F}$ = 241.1 Hz), 148.6, 143.4 (d, $^3J_{C-F}$ = 7.9 Hz), 142.3, 141.9, 140.56, 140.52, 140.45, 138.9 (d, $^4J_{C-F}$ = 2.3 Hz), 129.3, 128.0, 125.9 (d, $^3J_{C-F}$ = 8.8 Hz), 124.8, 120.7, 116.7, 116.5, 113.4 (d, $^2J_{C-F}$ = 22.9 Hz), 106.5 (d, $^2J_{C-F}$ = 23.0 Hz), 61.0, 36.8, 36.0, 14.4; IR (ATR-FTIR) 1709, 1609, 1407, 1251, 1121, 801, 751 cm^{-1}; MS (EI) m/z (%) 344 (M^+, 49), 316 (6), 299 (8), 271 (100), 200 (6), 149 (12), 135 (20), 59 (9); HRMS (EI-TOF) calcd for $C_{23}H_{17}FO_2$ (M^+) 344.1213, found 344.1217.

*Ethyl 9-fluoro-6,12-dihydroindeno[1,2-b]fluorene-3-carboxylate (**11c**).* In a 25 mL round-bottom flask, the solution of (*E*)-ethyl 3-(3-methyl-6-(trifluoromethyl)-9*H*-fluoren-2-yl)-4-(pyrrolidin-1-yldiazenyl)benzoate (**10c**) (325 mg, 0.66 mmol, 1.0 equiv) in toluene (5 mL) was stirred at room temperature, and then CF_3COOH (301 mg, 2.64 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The resulting reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **11c** (68 mg, 0.17 mmol, 26%) as a yellow solid: R_f = 0.45 (10:1 Petroleum ether/EtOAc); mp = 218−220 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1 H), 8.06−8.00 (m, 3 H), 7.98 (s, 1 H), 7.66−7.53 (m, 3 H), 4.44 (q, J = 7.2 Hz, 2 H), 4.02 (s, 4 H), 1.46 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.7, 147.2, 142.64, 142.57, 142.2, 141.8, 140.9, 140.0, 129.5 (q, $^2J_{C-F}$ = 31.5 Hz), 129.4, 128.1, 125.3, 124.9, 123.3 (q, $^3J_{C-F}$ = 3.9 Hz), 120.9, 116.9, 116.8, 116.5 (q, $^3J_{C-F}$ = 3.6 Hz), 61.0, 36.9, 36.8, 14.4; IR (ATR-FTIR) 1695, 1616, 1407, 1254, 1109, 823, 751 cm^{-1}; MS (EI) m/z (%) 394 (M^+, 100), 366 (16), 321 (54), 270 (7), 252 (69), 140 (13), 126 (26), 45 (6); HRMS (EI-TOF) calcd for $C_{24}H_{17}F_3O_2$ (M^+) 394.1181, found 394.1191.

F. Synthesis of 9,10-Dihydro-Phenanthrene Derivates.

F1. Procedure for Compound of 2-tert-Butylphenyl trifluoromethanesulfonate. A solution of 2-*tert*-butylphenol (1.502 g, 10 mmol, 1.0 equiv) in 20 mL of dry dichloromethane was chilled to 0 °C. Pyridine (1.20 mL, 15 mmol, 1.5 equiv) and trifluoromethanesulfonic anhydride (2.14 mL, 15.0 mmol, 1.5 equiv) were then added sequentially to the stirred solution. After the addition, the reaction mixture was warmed up to room temperature and stirred for 12 h until the phenol was fully consumed (monitored by TLC). The resulting reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave 2-*tert*-butylphenyl trifluoromethanesulfonate (2.577 g, 9.1 mmol, 91%) as light yellow oil.

*F2. Procedure for Compounds of **12b,c**. (E)-1-((2′-(tert-Butyl)-[1,1′-biphenyl]-2-yl)diazenyl)pyrrolidine (**12b**).* In a 50 mL Schlenck tube, 2-(*tert*-butyl)phenyl trifluoromethanesulfonate (564 mg, 2.12 mmol, 1.0 equiv), (E)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid (578 mg, 4.25 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (245 mg, 0.2 mmol, 0.1 equiv) and K_2CO_3 (881 mg, 6.37 mmol, 3.0 equiv) were dissolved in DMF (15 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 80 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **12b** (338 mg, 1.1 mmol, 51%) as brown oil: R_f = 0.57(10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 1 H), 7.40 (d, J = 8.4 Hz, 1 H), 7.32−7.18 (m, 3 H), 7.10 (t, J = 7.2 Hz, 2 H), 6.94 (d, J = 7.2 Hz, 1 H), 3.52 (br, 4 H), 1.90−1.79 (m, 4 H), 1.18 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 147.6, 140.0, 139.9, 132.7, 131.2, 127.5, 126.5, 126.3, 124.4, 123.8, 116.4, 36.5, 32.3, 23.7; IR (ATR-FTIR) 2959, 1474, 1414, 1321, 1106, 757 cm^{-1}; MS (EI) m/z (%) 307 (M^+, 28), 251 (16), 193 (31), 178 (88), 167 (100), 153 (100), 152 (100), 167 (100), 115 (19), 70 (28), 57 (42), 41 (37); HRMS (EI-TOF) calcd for $C_{20}H_{25}N_3$ (M^+) 307.2048, found 307.2053.

*(E)-Ethyl 2′-(tert-butyl)-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**12c**).* In a 50 mL Schlenck tube, 2-(*tert*-butyl)-phenyl trifluoromethanesulfonate (564 mg, 2.0 mmol, 1.0 equiv), (E)-5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenylboronic acid (1.164 g, 4.0 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (232 mg, 0.2 mmol, 0.1 equiv) and K_2CO_3 (830 mg, 6 mmol, 3.0 equiv) were dissolved in DMF (15 mL). The tube was filled with N_2 and sealed with a Teflon-lined cap at once. The reaction mixture was heated to 80 °C in an oil bath and stirred for 12 h. After the reaction mixture was cooled to room temperature, water (20 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **12c** (310 mg, 0.82 mmol, 41%) as a yellow solid: R_f = 0.34 (10:1 Petroleum ether/EtOAc); mp = 95−97 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.4 Hz, 2.0 Hz, 1 H), 7.93 (d, J = 2.0 Hz, 1 H), 7.54−7.45 (m, 2 H), 7.25 (dt, J = 7.8 Hz, 1.6 Hz, 1 H), 7.12 (t, J = 7.4 Hz, 1 H), 6.92 (dd, J = 7.6 Hz, 1.2 Hz, 1 H), 4.34 (q, J = 7.0 Hz, 2 H), 3.86 (br, 2 H), 3.18 (br, 2 H), 1.88 (br, 4 H), 1.36 (t, J = 7.2 Hz, 3 H), 1.17 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 152.5, 147.6, 139.7, 139.0, 132.7, 132.6, 129.1, 126.63, 126.59, 125.3, 124.5, 116.1, 60.6, 50.7, 46.2, 36.5, 32.4, 23.7, 23.2, 14.3; IR (ATR-FTIR) 1707, 1595, 1389, 1236, 1103, 750 cm^{-1}; MS (EI) m/z (%) 379 (M^+, 47), 334 (21), 235 (21), 225 (21), 209 (35), 193 (86), 178 (81), 167 (100), 152 (22), 70 (23), 57 (27), 41 (22); HRMS (EI-TOF) calcd for $C_{23}H_{29}N_3O_2$ (M^+) 379.2260, found 379.2260.

*F3. Procedure for Compounds of **13b,c**.* 9,9-Dimethyl-9,10-dihydrophenanthrene (**13b**). In a 25 mL round-bottom flask, the solution of (*E*)-1-((2′-(*tert*-butyl)-[1,1′-biphenyl]-2-yl)diazenyl)-pyrrolidine (**12b**) (215 mg, 0.7 mmol, 1.0 equiv) in toluene (4 mL) was stirred at room temperature, and then CF_3COOH (319 mg, 2.8 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was then heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10 mL) was added. The reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel

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chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **13a** (127 mg, 0.61 mmol, 87%) as a yellow solid: R_f = 0.74 (10:1 Petroleum ether/EtOAc); mp = 54−56 °C (recrystallized from EtOAc/Petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.30 (m, 2 H), 7.43−7.39 (m, 1 H), 7.33−7.27 (m, 3 H), 7.25−7.17 (m, 2 H), 2.78 (s, 2 H), 1.26 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 136.0, 134.2, 133.2, 128.6, 127.9, 127.4, 126.8, 126.5, 124.2, 124.1, 123.5, 44.0, 34.1, 27.9; IR (ATR-FTIR) 1485, 1446, 1285, 1088, 737 cm^{-1}; MS (EI) *m*/*z* (%) 208 (M^+, 14), 193 (100), 178 (62), 165 (20), 115 (10), 89 (12), 63 (14), 51 (13), 39 (23); HRMS (EI-TOF) calcd for $C_{16}H_{16}$ (M^+):208.1252, found 208.1248.

*Ethyl 9,9-dimethyl-9,10-dihydrophenanthrene-3-carboxylate (**13c**).* In a 25 mL round-bottom flask, the solution of (*E*)-ethyl 2′-(*tert*-butyl)-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (**12c**) (257 mg, 0.68 mmol, 1.0 equiv) in toluene (4 mL) was stirred at room temperature, and then CF_3COOH (310 mg, 2.72 mmol, 4.0 equiv) was added dropwise. The resulting reaction mixture was then heated to 100 °C and stirred for 1 h. After the reaction mixture was cooled to ambient temperature, $NaHCO_3$ solution (0.6 mol/L, 10.0 mL) was added. The reaction mixture was extracted with ethyl acetate (3 × 20 mL) and washed with water (20 mL) and brine (20 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography (1:20 to 1:10 EtOAc/Petroleum ether) gave **13c** (168 mg, 0.6 mmol, 88%) as a light yellow oil: R_f = 0.57 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.2 Hz, 1 H), 7.90 (dd, *J* = 7.8 Hz, 1.8 Hz, 1 H), 7.89−7.84 (m, 1 H), 7.45−7.40 (m, 1 H), 7.36−7.30 (m, 2 H), 7.26 (d, *J* = 6.8 Hz, 1 H), 4.41 (q, *J* = 7.1 Hz, 2 H), 2.83 (s, 2 H), 1.42 (t, *J* = 7.2 Hz, 3 H), 1.26 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.3, 141.3, 134.4, 132.4, 129.3, 128.7, 128.5, 126.7, 124.7, 124.4, 124.3, 60.9, 44.1, 34.1, 27.9, 14.4; IR (ATR-FTIR) 1714, 1609, 1365, 1239, 1105, 757 cm^{-1}; MS (EI) *m*/*z* (%) 280 (M^+, 54), 265 (7), 193 (100), 178 (19), 165 (10), 110 (6), 95 (6); HRMS (EI-TOF) calcd for $C_{19}H_{20}O_2$ (M^+) 280.1463, found 280.1461.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all 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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