Connecting Metalation and Intramolecular Inverse Diels–Alder Strategies of 1,2,4-Triazines: A Short and Efficient Synthesis of 1-Azafluorenones

Thomas Hundsdorf, Hans Neunhoeffer*

Darmstadt University of Technology, Institute of Organic Chemistry, Petersenstrasse 22, 64287 Darmstadt, Germany
Fax +49(6151) 163278; E-mail: di88@hrzpub.tu-darmstadt.de

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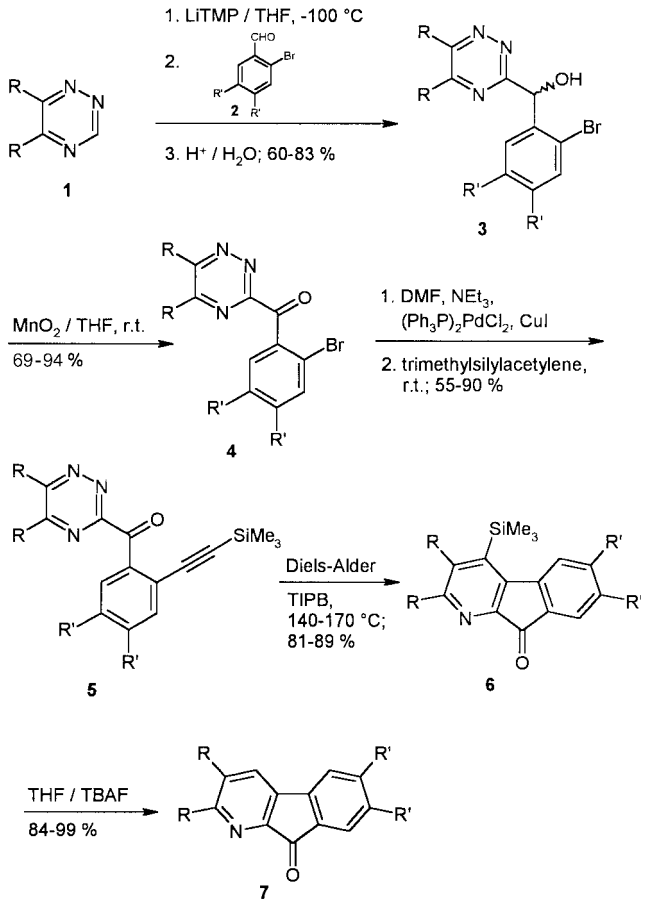
Abstract: A short high yield synthesis of polysubstituted 1-azafluorenones from 1,2,4-triazines using the metalation and intramolecular Diels–Alder reaction is described.

Key words: 1,2,4-triazines, π-deficient heterocycles, 1-azafluorenones, metalations, intramolecular Diels–Alder reactions

Studies aimed to establish synthetic links between metalation strategies and other prominent methods, e.g., transition metal catalyzed cross-coupling reactions[1] and olefin metathesis,[2] have been reported both in the field of carbo- and heteroaromatics for the construction of a variety of bioactive substances.[3,4] In the chemistry of π-deficient heterocycles, metalation[5] and inverse Diels–Alder strategies[6,7] are undoubtedly of high synthetic value. Surprisingly, no investigations have been undertaken to develop synthetic connections of the metalation and intramolecular inverse Diels–Alder reactions.

Based on our work on 1,2,4-triazines,[8,9] we reasoned that a synthetic link of metalation reactions to the intramolecular inverse Diels–Alder strategy may open a short pathway for the synthesis of condensed heterocyclic systems. In view of the natural occurrence and the biological activity of various fluorenones,[10,11] the azafluorenone system appeared an useful target for application of this concept. Starting from metalation of 1,2,4-triazines, we developed a short and efficient synthesis, which represents a practical synthetic protocol for polysubstituted 1-azafluorenones.

In a typical procedure, the 1,2,4-triazines **1** (**1a**,[14] **1b**[15]), when subjected to standard metalation with LiTMP at –100 °C, followed by the addition of several 2-bromobenzaldehydes **2**, afforded the benzylalcohols **3** (60–83% yield). Oxidation of **3** using MnO_2 in THF furnished the ketones **4** (69–94% yield). Subsequent Sonogashira coupling[12] of **4** under $PdCl_2(PPh_3)_2$–CuI catalyzed conditions led to **5**, which upon intramolecular Diels–Alder reaction in triisopropylbenzene (TIPB) gave the 4-trimethylsilyl-1-azafluorenones **6** in high yields (81–89%). Desilylation of **6** under TBAF-conditions resulted in the 1-azafluorenones **7** in excellent overall yields of 31–37%. The metalation products (benzylalcohols **3**),



Scheme

Diels–Alder precursors **5**, and final products **7** of this route are summarized in the Table.

To the best of our knowledge, there are only a few previous reports[13] on 1-azafluorenone syntheses. However, these methods need hard reaction conditions ($KMnO_4$, hot aqueous KOH;[13a-e] I_2O_5, hot aqueous KOH[13f]). As reported herein, our concept illustrates a new methodology for 1-azafluorenone ring formation, which, by virtue of its high overall yields, may complement and (or) supersede those classical methods.

In summary, a new and efficient synthetic route for the construction of 1-azafluorenones, based on metalation and intramolecular Diels–Alder reactions of 1,2,4-triazines has been developed. This procedure allows access to substituted systems, which are difficult to prepare by clas-

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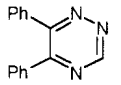
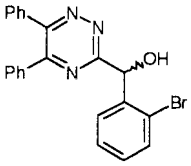
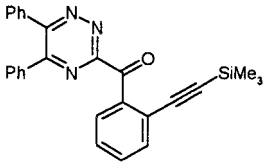
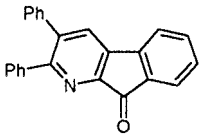
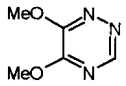
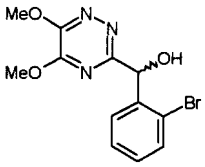
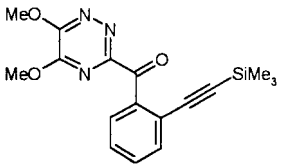
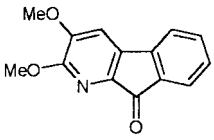
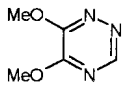
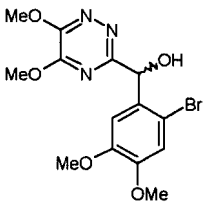
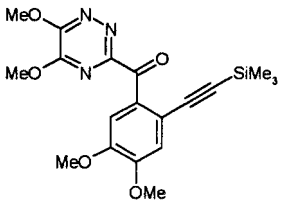
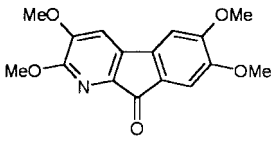
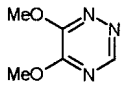
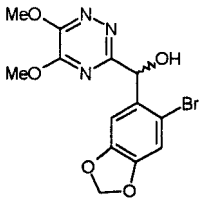
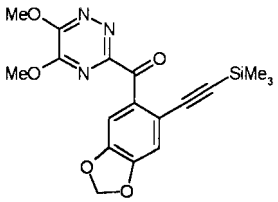
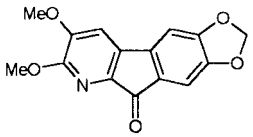
Table Metalation Products **3**, Intramolecular Inverse Diels–Alder Precursors **5**, and Final Products **7**

Entry	1,2,4-Triazine	Benzylalcohol	Alkyne	1-Azafluorenone	Overall Yield (%)
1	 **1a**[14]	 **3a**	 **5a**	 **7a**	36
2	 **1b**[15]	 **3b**	 **5b**	 **7b**	37
3	 **1b**[15]	 **3c**	 **5c**	 **7c**	31
4	 **1b**[15]	 **3d**	 **5d**	 **7d**	31

sical approaches. Further investigations on the synthesis of 2-azafluorenones are in progress and will be reported in due course.

Metalation experiments were carried out under Ar in THF, which was freshly distilled from sodium benzophenone ketyl under Ar prior to use. Solvents used in all other experiments (oxidation, Sonogashira coupling, Diels–Alder reaction, desilylation) were dried over molecular sieves. IR spectra were obtained on a Nicolet impact 400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 or ARX-300 spectrometer. MS were determined on a Varian 212 instrument at 70 eV. Elemental analysis were obtained on a Perkin-Elmer CHN 240 A or 240 B.

3-(2-Bromo-α-hydroxybenzyl)-1,2,4-triazines 3; General Procedure

To cooled (–60 °C) THF (40 mL) were added 2,2,6,6-tetramethylpiperidine (TMPH) (0.80 mL, 4.7 mmol) and 2.5 M *n*-BuLi solution (1.60 mL, 4.0 mmol). The mixture was allowed to warm to r.t., stirred for 30 min, and cooled to –100 °C. The 1,2,4-triazine **1**[14,15] (1.0 mmol) in THF (5 mL) was added in portions while keeping the internal temperature below –95 °C. After 3–10 min (accumulation time; t_A), 2-bromobenzaldehyde **2** (4.0 mmol) was added and the solution was stirred for 60 min (T ≤ –95 °C). The mixture was treated with concd HCl–MeOH–THF (1:1:4) (4.5 mL), and allowed to warm to r.t. Saturated $NaHCO_3$ was added until pH 8, the organic solvent was removed under vacuum (40 °C), and the remaining solution extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), the solvent removed under vacuum, and the crude residue purified as specified below.

3-(2-Bromo-α-hydroxybenzyl)-5,6-diphenyl-1,2,4-triazine (3a)

t_A = 3.5 min; column chromatography (cyclohexane–EtOAc, 2:1); light yellow crystals; yield: 60%.

Mp 118 °C.

IR (KBr): 3206, 3058, 2926, 1505, 1449, 1388, 1016, 756, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.20 (s, 1 H, OH), 6.56 (s, 1 H, CH-OH), 7.11 (m, 1 H, Ph), 7.32 (m, 7 H, Ph), 7.51 (m, 6 H, Ph).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 74.12, 123.87, 127.84, 128.68, 128.82, 129.31, 129.60, 129.80, 130.02, 130.14, 131.34, 133.26, 135.02, 135.14, 140.26, 156.26, 156.77, 165.64.

EIMS: *m/z* (%) = 419 (M^+, 1; ^{81}Br), 417 (M^+, 1; ^{79}Br), 338 (73), 178 (100), 152 (9), 77 (9).

Anal. Calcd for $C_{22}H_{16}BrN_3O$: C, 63.17; H, 3.86; N, 10.05. Found: C, 63.43; H, 3.95; N, 9.97.

3-(2-Bromo-α-hydroxybenzyl)-5,6-dimethoxy-1,2,4-triazine (3b)
t_A = 10 min; column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 83%.

Mp 88–89 °C.

IR (KBr): 3267, 3030, 2956, 2921, 1551, 1510, 1403, 1255, 1011, 746, 593 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, OMe), 4.08 (s, 3 H, OMe), 4.45 (s, 1 H, OH), 6.22 (s, 1 H, CH-OH), 7.07 (m, 1 H, Ar-H), 7.22 (m, 1 H, Ar-H), 7.39 (m, 1 H, Ar-H), 7.49 (m, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.10, 55.54, 73.36, 123.77, 127.69, 128.85, 129.53, 132.97, 140.47, 154.55, 155.23, 161.57.

FDMS: *m/z* (%) = 328 (M^+ +1, 43; ^{81}Br), 326 (M^+ +1, 37; ^{79}Br), 246 (100), 43 (16).

Anal. Calcd for $C_{12}H_{12}BrN_3O_3$: C, 44.19; H, 3.71; N, 12.88. Found: C, 44.16; H, 3.72; N, 12.81.

3-(2-Bromo-α-hydroxy-4,5-dimethoxybenzyl)-5,6-dimethoxy-1,2,4-triazine (3c)
t_A = 10 min; column chromatography (cyclohexane–EtOAc, 1:2); colorless crystals; yield: 68%.

Mp 102 °C.

IR (KBr): 3420, 3007, 2951, 2849, 1551, 1500, 1403, 1266, 1159, 1026, 991, 731, 594 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 4.09 (s, 3 H, OMe), 4.52 (s, 1 H, OH), 6.14 (s, 1 H, CH-OH), 6.93 (s, 1 H, Ar-H), 6.95 (s, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.19, 55.57, 56.12, 56.24, 73.13, 110.78, 113.70, 115.33, 132.23, 148.76, 149.32, 154.53, 155.38, 161.80.

EIMS: *m/z* (%) = 387 (M^+, 1; ^{81}Br), 385 (M^+, 1; ^{79}Br), 306 (100), 274 (13), 168 (22), 140 (17).

Anal. Calcd for $C_{14}H_{16}BrN_3O_5$: C, 43.54; H, 4.18; N, 10.88. Found: C, 43.50; H, 4.04; N, 11.13.

3-(2-Bromo-α-hydroxy-4,5-methylenedioxybenzyl)-5,6-dimethoxy-1,2,4-triazine (3d)
t_A = 5 min; 6-bromopiperonal (4.5 mmol); column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 71%.

Mp 130–131 °C.

IR (KBr): 3414, 3007, 2956, 2905, 1551, 1499, 1480, 1398, 1235, 1113, 1037, 934, 843, 568 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.03 (s, 3 H, OMe), 4.16 (s, 3 H, OMe), 4.33 (s, 1 H, OH), 5.95 (d, 2 H, ^2J = 1.3 Hz), 6.22 (s, 1 H, CH-OH), 6.92 (s, 1 H, Ar-H), 7.01 (s, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 55.10, 55.54, 73.20, 101.92, 108.33, 112.68, 114.39, 133.73, 147.76, 148.23, 154.59, 155.37, 161.68.

FDMS: *m/z* (%) = 371 (M^+, 90; ^{81}Br), 369 (M^+, 100; ^{79}Br).

Anal. Calcd for $C_{13}H_{12}BrN_3O_5$: C, 42.19; H, 3.27; N, 11.35. Found: C, 42.39; H, 3.35; N, 11.09.

3-(2-Bromobenzoyl)-1,2,4-triazines 4; General Procedure
To a solution of **3** (0.5 mmol) in THF (20 mL) was added MnO_2 (0.87 g, 10.0 mmol), and the suspension was stirred at r.t. for 5 h. The mixture was filtrated, the solvent evaporated under vacuum, and the crude residue was purified as specified below.

3-(2-Bromobenzoyl)-5,6-diphenyl-1,2,4-triazine (4a)
Column chromatography (cyclohexane–EtOAc, 2:1); light yellow crystals; yield: 93%.

Mp 165 °C.

IR (KBr): 3078, 3058, 1709, 1495, 1439, 1368, 1286, 1205, 1093, 1006, 853, 761, 751, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (m, 8 H, Ar-H), 7.58 (m, 5 H, Ar-H), 7.62 (m, 1 H, Ar-H).

EIMS: *m/z* (%) = 417 (M^+, 1; ^{81}Br), 415 (M^+, 1; ^{79}Br), 336 (90), 178 (100), 155 (14), 76 (13).

Anal. Calcd for $C_{22}H_{14}BrN_3O$: C, 63.48; H, 3.39; N 10.09. Found: C, 63.44; H, 3.33; N, 10.04.

3-(2-Bromobenzoyl)-5,6-dimethoxy-1,2,4-triazine (4b)
Column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 77%.

Mp 147–148 °C.

IR (KBr): 3027, 2966, 1704, 1576, 1546, 1500, 1408, 1377, 1265, 1214, 991, 889, 766, 700, 624 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.15 (s, 3H, OMe), 4.17 (s, 3H, OMe), 7.34 (m, 2H, Ar-H), 7.52 (m, 2H, Ar-H).

EIMS: *m/z* (%) = 324 (M^+–1, 1; ^{81}Br), 322 (M^+–1, 1; ^{79}Br), 244 (100), 201 (15), 185 (65), 183 (64), 159 (54), 157 (59), 155 (60), 144 (16), 86 (22), 76 (54), 75 (52), 50 (39), 43 (41).

Anal. Calcd for $C_{12}H_{10}BrN_3O_3$: C, 44.47; H, 3.11; N, 12.96. Found: C, 44.24; H, 3.12; N, 12.78.

3-(2-Bromo-4,5-dimethoxybenzoyl)-5,6-dimethoxy-1,2,4-triazine (4c)
Column chromatography (cyclohexane–EtOAc, 1:2); yellow crystals; yield: 94%.

Mp 173–174 °C.

IR (KBr): 3058, 3002, 2966, 2839, 1688, 1602, 1571, 1546, 1510, 1403, 1398, 1261, 1204, 1174, 1026, 991, 853, 777, 619 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 4.14 (s, 3 H, OMe), 4.18 (s, 3 H, OMe), 6.97 (s, 1 H, Ar-H), 7.14 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 386 (M^++1, 1; ^{81}Br), 384 (M^++1, 1; ^{79}Br), 304 (100), 243 (12), 204 (13).

Anal. Calcd for $C_{14}H_{14}BrN_3O_5$: C, 43.77; H, 3.67; N 10.94. Found: C, 43.96; H, 3.74; N, 10.95.

3-(2-Bromo-4,5-methylenedioxybenzoyl)-5,6-dimethoxy-1,2,4-triazine (4d)
Column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 69%.

Mp 147–148 °C.

IR (KBr): 3053, 3007, 2956, 2910, 1688, 1617, 1545, 1505, 1480, 1398, 1250, 1133, 1031, 1001, 863, 782, 588 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.14 (s, 3 H, OMe), 4.18 (s, 3 H, OMe), 5.99 (s, 2 H, O-CH_2-O), 6.97 (s, 1 H, Ar-H), 7.03 (s, 1 H, Ar-H).

FDMS: *m/z* (%) = 369 (M^+, 72; ^{81}Br), 367 (M^+, 100; ^{79}Br), 144 (12).

Anal. Calcd for $C_{13}H_{10}BrN_3O_5$: C, 42.42; H, 2.74; N, 11.41. Found: C, 42.42; H, 2.79; N, 11.60.

3-[2-(Trimethylsilylethynyl)-benzoyl]-1,2,4-triazines 5; General Procedure
To a solution of **4** (0.25 mmol) in DMF (2.0 mL) and Et_3N (2.0 mL) were added CuI (2.0 mg, 11 μmol) and $PdCl_2(PPh_3)_2$ (7.0 mg, 10

μmol), and the solution was stirred for 20 min at r.t. Then, trimethylsilylacetylene (70 μL, 0.50 mmol) was added, and the mixture stirred for 3–7 h (TLC control) at r.t. H_2O (10 mL) and Et_2O (10 mL) were added, and the reaction mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were separated, dried ($MgSO_4$), and purified as specified below to afford **5**.

5,6-Diphenyl-3-[2-(trimethylsilylethynyl)-benzoyl]-1,2,4-triazine (5a)
Column chromatography (cyclohexane–EtOAc, 2:1); yellow crystals; yield: 82%.

Mp 138–139 °C.

IR (KBr): 3058, 2961, 2895, 2157, 1688, 1602, 1495, 1454, 1378, 1250, 1199, 1011, 879, 843, 777, 711 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = –0.15 (s, 9 H, $SiMe_3$), 7.37 (m, 9 H, Ar-H), 7.57 (m, 4 H, Ar-H), 7.76 (m, 1 H, Ar-H).

EIMS: *m/z* (%) = 433 (M^+, 21), 405 (40), 390 (24), 336 (10), 201 (10), 178 (100), 73 (16).

HRMS: *m/z* calcd. for $C_{27}H_{23}N_3OSi$: 433.1610. Found: 433.1644.

5,6-Dimethoxy-3-[2-(trimethylsilylethynyl)-benzoyl]-1,2,4-triazine (5b)
Column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 85%.

Mp 104–105 °C.

IR (KBr): 3073, 3012, 2956, 2895, 2162, 1693, 1545, 1500, 1403, 1255, 996, 909, 843, 767, 619 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = –0.07 (s, 9 H, $SiMe_3$), 4.24 (s, 3 H, OMe), 4.29 (s, 3 H, OMe), 7.50 (m, 3 H, Ar-H), 7.76 (m, 1 H, Ar-H).

EIMS: *m/z* (%) = 341 (M^+, 72), 326 (91), 310 (100), 298 (61), 244 (51), 201 (36), 187 (33), 143 (57), 89 (39), 73 (27), 43 (61).

HRMS: *m/z* calcd. for $C_{17}H_{19}N_3O_3Si$: 341.1196. Found: 341.1188.

5,6-Dimethoxy-3-[4,5-dimethoxy-2-(trimethylsilylethynyl)-benzoyl]-1,2,4-triazine (5c)
Column chromatography (cyclohexane–EtOAc, 2:1); yellow crystals; yield: 55%.

Mp 50–51 °C.

IR (KBr): 3084, 3002, 2996, 2931, 2859, 2152, 1683, 1597, 1541, 1495, 1398, 1271, 1138, 1001, 858, 751, 599 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, $SiMe_3$), 3.95 (s, 3 H, OMe), 3.98 (s, 3 H, OMe), 4.18 (s, 3 H, OMe), 4.24 (s, 3 H, OMe), 6.96 (s, 1 H, Ar-H), 7.39 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 401 (M^+, 52), 386 (75), 373 (71), 370 (100), 358 (49), 343 (15), 328 (18), 312 (14), 304 (14), 295 (12), 272 (12), 261 (44), 228 (12), 203 (20), 169 (12), 123 (17), 89 (32), 73 (40).

HRMS: *m/z* calcd. for $C_{19}H_{23}N_3O_5Si$: 401.1407. Found: 401.1382.

5,6-Dimethoxy-3-[4,5-methylenedioxy-2-(trimethylsilylethynyl)-benzoyl]-1,2,4-triazine (5d)
Column chromatography (cyclohexane–EtOAc, 1:1); colorless crystals; yield: 90%.

Mp 144–145 °C.

IR (KBr): 3084, 3017, 2971, 2956, 2147, 1693, 1541, 1495, 1393, 1250, 1128, 1031, 996, 858, 594 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 4.19 (s, 3 H, OMe), 4.25 (s, 3 H, OMe), 6.08 (s, 2 H, O-CH_2-O), 6.95 (s, 1 H, Ar-H), 7.30 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 385 (M^+, 100), 370 (82), 354 (100), 342 (67), 311 (15), 288 (50), 256 (17), 245 (36), 231 (16), 187 (20), 115 (37), 89 (18), 73 (35), 43 (41).

HRMS: *m/z* calcd. for $C_{18}H_{19}N_3O_5Si$: 385.1094. Found: 385.1139.

4-Trimethylsilyl-1-azafluorenones 6; General Procedure
A solution of the alkyne **5** (0.15 mmol) in triisopropylbenzene (TIPB) (3 mL) was heated until the reaction was complete (TLC control). The mixture was cooled, the solvent removed under high vacuum (0.1 mbar), and the crude residue purified as specified below.

2,3-Diphenyl-4-trimethylsilyl-1-azafluorenone (6a)
The mixture was heated to 140 °C (1 h); column chromatography (cyclohexane–EtOAc, 2:1); yellow crystals; yield: 83%.

Mp 220–221 °C.

IR (KBr): 3063, 3053, 2951, 1724, 1607, 1546, 1347, 1255, 1184, 970, 869, 762, 716 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9 H, $SiMe_3$), 7.14 (m, 10 H, Ar-H), 7.30 (m, 1 H, Ar-H), 7.49 (m, 1 H, Ar-H), 7.63 (m, 1 H, Ar-H), 7.72 (m, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.36, 124.59, 126.19, 127.46, 127.53, 128.09, 128.16, 129.41, 129.98, 131.33, 133.37, 134.66, 139.92, 141.09, 143.93, 145.14, 145.75, 145.92, 150.79, 157.87, 192.89.

EIMS: *m/z* (%) = 405 (M^+, 88), 390 (99), 332 (36), 178 (48), 73 (100), 45 (28).

Anal. Calcd for $C_{27}H_{23}NOSi$: C, 79.96; H, 5.72; N, 3.45. Found: C, 79.77; H, 5.84; N, 3.25.

2,3-Dimethoxy-4-trimethylsilyl-1-azafluorenone (6b)
The mixture was heated to 170 °C (1.5 h); column chromatography (cyclohexane–EtOAc, 5:1); light orange crystals; yield: 83%.

Mp 131–132 °C.

IR (KBr): 3084, 3017, 2982, 2946, 2900, 1724, 1608, 1520, 1459, 1383, 1347, 1266, 1123, 1001, 853, 772, 731 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 9 H, $SiMe_3$), 3.79 (s, 3 H, OMe), 4.03 (s, 3 H, OMe), 7.14 (m, 1 H, Ar-H), 7.35 (m, 2 H, Ar-H), 7.56 (m, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.56, 54.22, 60.99, 124.10, 124.25, 128.20, 133.14, 134.32, 137.26, 141.52, 143.03, 144.45, 152.19, 158.16, 192.18.

EIMS: *m/z* (%) = 313 (M^+, 100), 298 (29), 270 (11), 255 (20), 240 (19), 225 (29), 212 (11), 197 (17), 89 (23), 73 (84), 59 (37), 45 (22).

Anal. Calcd for $C_{17}H_{19}NO_3Si$: C, 65.15; H, 6.11; N, 4.47. Found: C, 64.89; H, 5.89; N, 4.19.

2,3,6,7-Tetramethoxy-4-trimethylsilyl-1-azafluorenone (6c)
The mixture was heated to 150 °C (1.5 h); column chromatography (cyclohexane–EtOAc, 3:1); orange-red crystals; yield: 89%.

Mp 154–155 °C.

IR (KBr): 3007, 2956, 2900, 2859, 2839, 1725, 1597, 1505, 1464, 1373, 1240, 1093, 1016, 873, 756, 675, 568 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.48 (s, 9 H, $SiMe_3$), 3.77 (s, 3 H, OMe), 3.85 (s, 3 H, OMe), 3.88 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 7.00 (s, 1 H, Ar-H), 7.14 (s, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.82, 54.17, 56.40, 56.41, 60.94, 107.82, 108.94, 126.19, 136.00, 137.96, 140.67, 145.15, 148.71, 151.65, 153.64, 157.48, 191.48.

EIMS: *m/z* (%) = 373 (M^+, 100), 358 (12), 73 (28).

Anal. Calcd for $C_{19}H_{23}NO_5Si$: C, 61.10; H, 6.21; N, 3.75. Found: C, 60.85; H, 6.00; N, 3.71.

2,3-Dimethoxy-6,7-methylenedioxy-4-trimethylsilyl-1-azafluorenone (6d)
The mixture was heated to 150 °C (0.75 h); column chromatography (cyclohexane–EtOAc, 3:1); red crystals; yield: 81%.

Mp 185–186 °C.

IR (KBr): 3099, 3017, 2961, 2931, 2900, 1729, 1607, 1515, 1474, 1373, 1230, 1026, 869, 762, 650 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.43 (s, 9 H, $SiMe_3$), 3.76 (s, 3 H, OMe), 4.14 (s, 3 H, OMe), 5.98 (s, 2 H, O-CH_2-O), 6.90 (s, 1 H, Ar-H), 7.04 (s, 1 H, Ar-H).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 1.70, 54.22, 61.00, 102.27, 105.56, 106.44, 127.74, 136.49, 140.10, 140.44, 144.95, 147.18, 151.67, 152.66, 157.46, 190.75.

EIMS: *m/z* (%) = 357 (M^+, 100), 327 (11), 223 (11), 73 (32), 59 (12).

Anal. Calcd for $C_{18}H_{19}NO_5Si$: C, 60.51; H, 5.36; N, 3.92. Found: C, 60.24; H, 5.16; N, 3.84.

1-Azafluorenones 7; General Procedure
To a solution of **6** (0.10 mmol) in THF (10 mL) was added tetrabutylammoniumfluoride (TBAF) on silica gel (1.1 mmol F^-/g silica gel; 112 mg, 0.123 mmol) and the solution was stirred for 3 h. The silica gel was separated by filtration, H_2O (3 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent removed in vacuum. The crude product was chromatographed as specified below.

2,3-Diphenyl-1-azafluorenone (7a)
Column chromatography (cyclohexane–EtOAc, 1:1); yellow crystals; yield: 94%.

Mp 192–193 °C.

IR (KBr): 3084, 3058, 3033, 1729, 1592, 1403, 1184, 955, 767, 706 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.24 (m, 11 H, Ar-H), 7.50 (m, 2 H, Ar-H), 7.71 (m, 1 H, Ar-H), 7.80 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 333 (M^+, 86), 332 (M^+ - 1, 100), 303 (16), 276 (13), 166 (10), 152 (16).

Anal. Calcd for $C_{24}H_{15}NO$: C, 86.46; H, 4.54; N, 4.20. Found: C, 86.45; H, 4.50; N, 3.99.

2,3-Dimethoxy-1-azafluorenone (7b)
Column chromatography (cyclohexane–EtOAc, 1:1); yellow-orange crystals; yield: 84%.

Mp 197 °C.

IR (KBr): 3099, 3073, 3017, 2941, 2859, 1714, 1607, 1581, 1480, 1408, 1368, 1271, 1225, 1128, 1021, 802, 726 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.96 (s, 3 H, OMe), 4.06 (s, 3 H, OMe), 7.10 (s, 1 H, Ar-H), 7.17 (m, 1 H, Ar-H), 7.25 (m, 1 H, Ar-H), 7.36 (m, 1 H, Ar-H), 7.51 (m, 1 H, Ar-H).

EIMS: *m/z* (%) = 241 (M^+, 100), 226 (25), 212 (58), 198 (17), 170 (33), 155 (30), 147 (18), 127 (43), 76 (13).

Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.71; H, 4.60; N, 5.80. Found: C, 69.67; H, 4.61; N, 5.61.

2,3,6,7-Tetramethoxy-1-azafluorenone (7c)
Column chromatography (CH_2Cl_2–EtOAc, 1:1); light red crystals; yield: 99%.

Mp 209 °C.

IR (KBr): 3073, 3007, 2992, 2941, 2849, 1704, 1607, 1576, 1480, 1408, 1250, 1098, 991, 767, 604 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3 H, OMe), 4.01 (s, 3 H, OMe), 4.02 (s, 3 H, OMe), 4.11 (s, 3 H, OMe), 6.86 (s, 1 H, Ar-H), 7.08 (s, 1 H, Ar-H), 7.19 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 301 (M^+, 100), 286 (22), 215 (11).

Anal. Calcd for $C_{16}H_{15}NO_5$: C, 63.79; H, 5.02; N, 4.64. Found: C, 63.70; H, 5.27; N, 4.36.

2,3-Dimethoxy-6,7-methylenedioxy-1-azafluorenone (7d)
Column chromatography (CH_2Cl_2–EtOAc, 1:1); light red crystals; yield: 88%.

Mp >300 °C.

IR (KBr): 3078, 3012, 2982, 2946, 1709, 1576, 1480, 1413, 1261, 1220, 1062, 1037, 884, 792 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.00 (s, 3 H, OMe), 4.10 (s, 3 H, OMe), 6.04 (s, 2 H, O-CH_2-O), 6.81 (s, 1 H, Ar-H), 7.02 (s, 1 H, Ar-H), 7.08 (s, 1 H, Ar-H).

EIMS: *m/z* (%) = 285 (M^+, 100), 270 (10), 256 (27), 242 (21), 214 (28), 199 (29).

Anal. Calcd for $C_{15}H_{11}NO_5$: C, 63.16; H, 3.89; N, 4.91. Found: C, 63.31; H, 3.86; N, 4.80.

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