DOI: 10.1002/ejoc.200500926

Synthesis of the Benzo[*b*]fluorene Core of the Kinamycins by Arylalkyne–Allene and Arylalkyne–Alkyne Cycloadditions

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Keywords: Quinones / Cycloadditions / Alkynes / Allenes / Natural products

Arylalkyne–allene and arylalkyne–alkyne cycloadditions yields benzo[*a*]fluorenones, which are related to the tetracyclic core of the kinamycins. In the arylalkyne–alkyne cycloadditions, we found a rearrangement that produces benzo[*a*]fluorenones, in addition to the expected benzo[*b*]fluorenones. This rearrangement could be suppressed in the presence of phenol, which allowed the synthesis of 4,9-dimethoxy-2-methyl-11*H*-benzo[*b*]fluoren-11-one in excellent yield.

Introduction

The kinamycins (**1**) are antibiotics originally isolated from *Streptomyces murayamaensis* by Omura in 1970 (Figure 1).[1] Although the kinamycins were characterized as *N*-cyanobenzo[*b*]carbazoles, they were later redefined as diazoparaquinones,[2] following our synthesis of **2**, with the structure originally assigned to prekinamycin.[3,4] Prekinamycin was shown to be diazobenzo[*b*]fluorene quinone **3**.[5,6] Kinafluorenone (**4**)[7] and stealthin A (**5**),[8] are other representative benzo[*b*]fluorene natural products structurally related to the kinamycins. Interestingly, isoprekinamycin, originally assigned as a diazobenzo[*b*]fluorene,[1] was also reassigned to the diazobenzo[*a*]fluorene derivative **6**.[5] The fluostatins A (**7**) and B (**8**) are also naturally occurring benzo[*a*]fluorenes.[9]

In addition to having antibacterial properties, some of the kinamycins show antitumor activity, which has been attributed to the loss of dinitrogen from the diazo group to generate a radical intermediate that induces DNA cleavage.[10,11] This loss of dinitrogen is probably initiated by a one-electron addition to the *p*-quinone.[12] Lomaiviticins A (**9**) and B (**10**) are particularly interesting dimeric compounds, as they show very potent antitumor activity, in addition to antibacterial activity against *Staphylococcus aureus*.[13]

The novel structures and antitumor activities of the kinamycins have stimulated the interest for the development of their total synthesis. Hauser completed an efficient synthesis of compound **3**.[14] A similar approach for the synthesis of the kinafluorene skeleton has been published.[15] Gould[5] and Kamikawa[16] completed the synthesis of the stealthins. A formal synthesis of the stealthins was also reported by Snieckus.[17] Other work, directed towards the synthesis of the more simple members of this family, have been reported.[18–21] However, thus far, only one approach for the synthesis of the more functionalized kinamycins (**1**) has been reported.[22]

We approached the synthesis of the benzo[*b*]fluorene core of the kinamycins by the arylalkyne–allene cycloaddition,[23] which was inspired by the [4+2] cycloaddition of arylalkyne–allenes developed by Schmittel.[24,25] As the thermal reaction of enynes with alkynes also leads to annulation,[26] we decided to explore in parallel this approach, which is based on the arylalkyne–alkyne cycloaddition.[27] Saá and co-workers have extensively studied similar arylalkyne–alkyne cycloadditions.[28,29] In this paper, we report full details of our work, directed towards the synthesis of kinamycins based on the intramolecular reaction of arylalkynes with allenes or alkynes.

Results and Discussion

Cycloaddition Arylalkyne/Allene

We decided to access to target **3** through the retrosynthetic plan outlined in Scheme 1. Thus, compound **3** could be available from compound **11** by the benzylic oxidation and oxidation of the B ring to the *p*-quinone. Intermediate **11** could be assembled by the arylalkyne/allene intramolecular cycloaddition of **12**. The allene moiety of **12** could be introduced by a [2,3]-sigmatropic rearrangement of the propargyl alcohol **13**, which could be constructed by the

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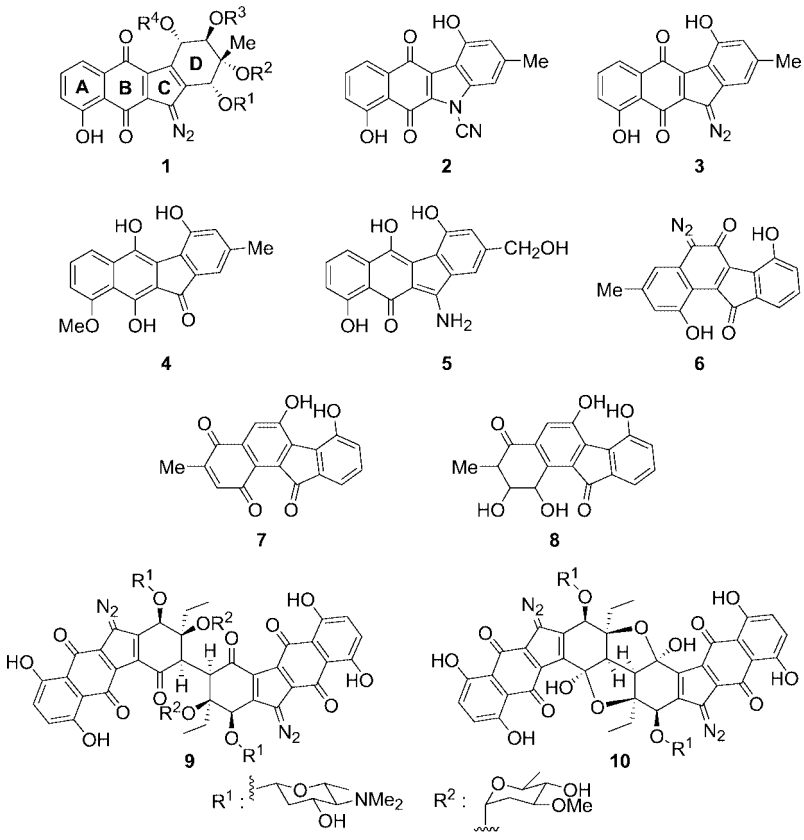
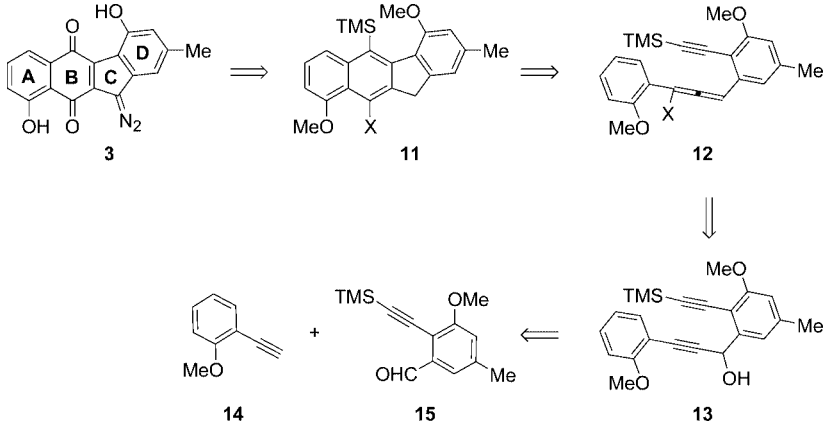


Figure 1. Kinamycins and related naturally occurring compounds.

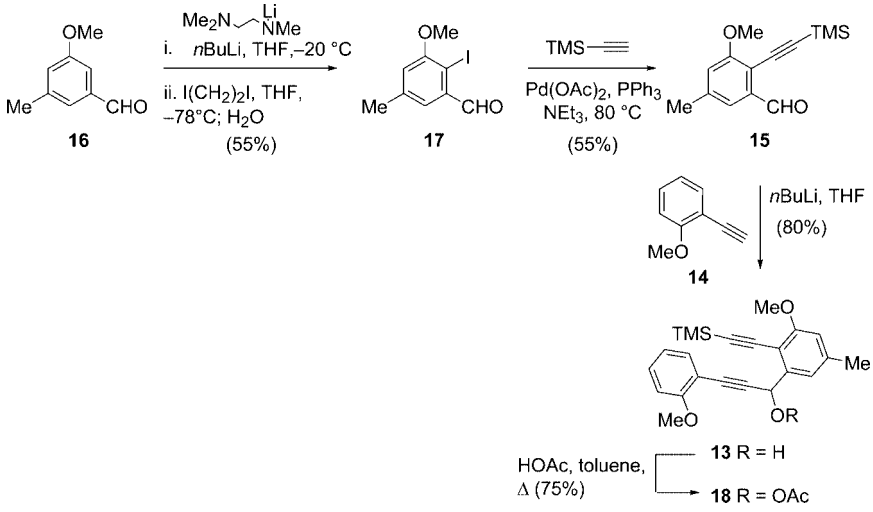
addition of the lithium acetylide of **14** to the benzaldehyde **15**.

The benzaldehyde **15** was prepared in two steps from **16** (Scheme 2). Thus, *o*-lithiation of **16** with lithium *N*,*N*,*N*′-trimethylethylenediamide and *n*BuLi,[30] followed by trapping of the lithium derivative with 1,2-diiodoethane[31] yields compound **17** in 55% yield. Sonogashira coupling of the aryl iodide **17** with (trimethylsilyl)acetylene gave **15** in 54% yield. Addition of the lithium acetylide of **14** to the aldehyde **15** provided the alcohol **13** in 80% yield. The propargyl alcohol **13** led only to the acetate **18** in 75% yield after being heated in toluene under reflux in the presence of HOAc.

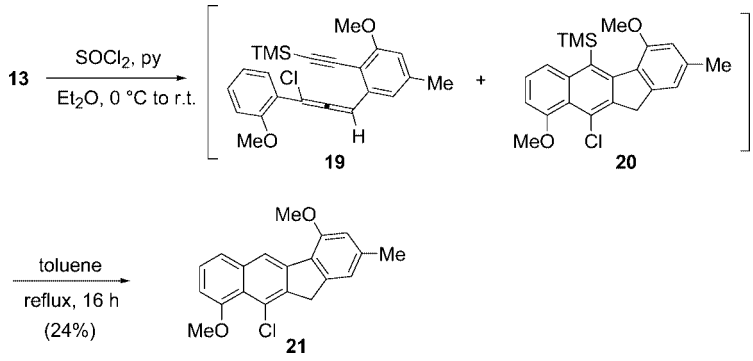
Thionyl chloride has been reported to promote reaction cascades similar to those required for the synthesis of **3** (Scheme 1).[32] In the event, when the propargyl alcohol **13** was treated with thionyl chloride in the presence of pyridine in anhydrous Et_2O, the initially formed chlorosulfite undergoes a S_Ni' reaction to form the chlorinated allene **19** (Scheme 3). Indeed, the allene **19** and the cyclized product **20** were detected in the ^1H NMR of the crude reaction mixture. When this mixture was heated in toluene under



Scheme 1.



Scheme 2.



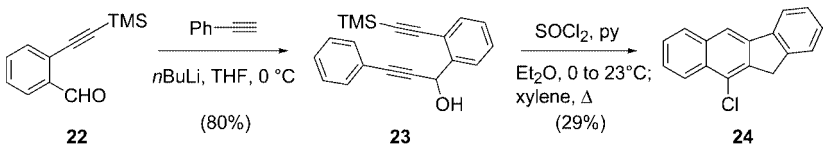
Scheme 3.

reflux, the desilylated tetracyclic chloride **21** was obtained as the only compound, albeit the isolated yield was low (24%).

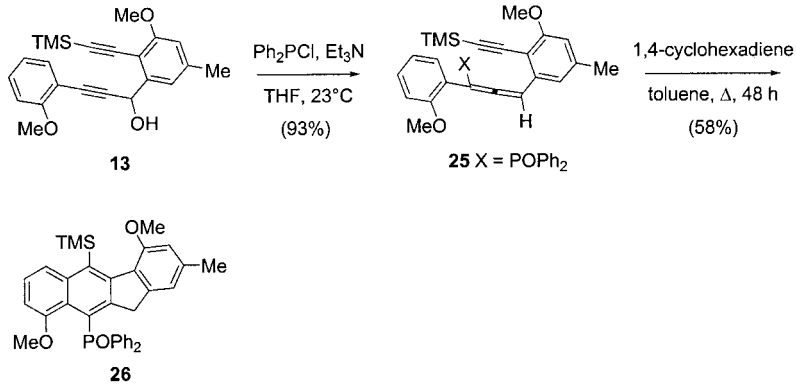
We also obtained a very similar result in the cyclization of a simple model system (Scheme 4). Thus, reaction between the known compound **22**[33] and lithium phenylacetylide gave the alcohol **23** in 80% yield. Reaction of **23** with thionyl chloride and pyridine, followed by heating of the crude mixture in xylene under reflux furnished the desilylated **24** in 29%.

Because of the low yields achieved in the cyclizations of **13** and **23** initiated by reaction with thionyl chloride, we decided to try the preparation of different allenes by the [2,3]-sigmatropic rearrangement of the appropriate *O*-derivatized alcohols. Thus, reaction of **13** with Ph_2PCl and NEt_3 in THF led to clean formation of the allene **25** by phosphorylation of the alcohol, followed by [2,3]-sigmatropic rearrangement (Scheme 5).[34] The allene **25** is stable at room temperature, but it undergoes smooth cycloaddition–aromatization after being heated in toluene in the presence of an excess of 1,4-cyclohexadiene to give the benzo[*b*]fluorene **26** as the major compound in 58% yield. The tetracyclic compound **26** possesses the skeleton of the kinamicins. 1,4-Cyclohexadiene was added to facilitate aromatization of the initially formed tetracyclic intermediate. However, somewhat surprisingly, in the absence of the 1,4-cyclohexadiene, compound **25** was recovered unchanged after being heated in toluene for 5 days. Reaction of **13** with phenylsulfenyl chloride and NEt_3 failed to give the corresponding allenyl sulfoxide.

Unfortunately, oxidation of the B ring of **21** (see Scheme 3) or **26** with a variety of reagents [$Pb(OAc)_4$, CrO_3, CAN] led to the oxidation of the A and/or D rings. Similarly, attempted substitution of the TMS of **26** by a trifluoroacetoxy group with $Pb(OCOCF_3)_4$ in CF_3COOH[35] led only to desilylation.



Scheme 4.



Scheme 5.

Cycloaddition Arylalkyne/Alkyne

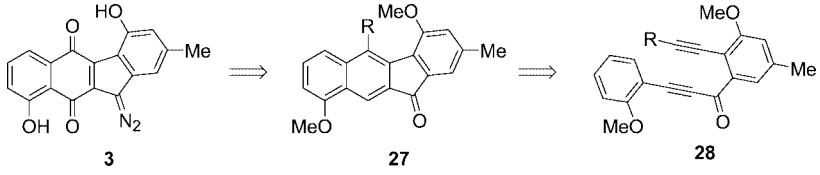
An alternative approach for the synthesis of **3** and related compounds, is outlined in Scheme 6. In this case, the intermediate **27** has the correct oxidation state at the C ring. The key cycloadditions were expected to take place from ynones of type **28**.

The model substrates **33**–**37** were readily assembled in two steps by the reaction of the benzaldehyde **22**[33] with the corresponding lithium arylacetylides, followed by oxidation of the alcohols **23**–**32** with $BaMnO_4$ (Scheme 7).

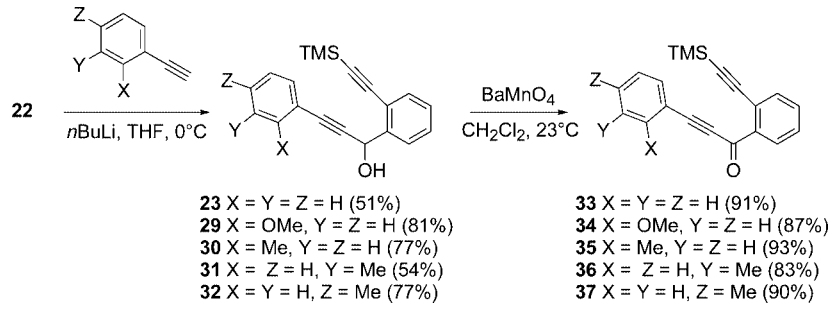
The cyclizations of **33**–**37** were best carried out by heating 0.06–0.2 M solutions in 1,2-dichlorobenzene under reflux (180 °C) (method A). Alternatively, the reactions could also be carried out in the solid state as a dispersion in celite (method B), or in toluene in a sealed tube (method C). Under these conditions, benzylated derivatives were obtained as byproducts as a result of hydrogen abstraction from toluene followed by radical coupling. Following method C γ-terpinene was added as a high-boiling 1,4-cyclohexadiene to facilitate hydrogen migration in the final aromatization step.

In addition to the expected benzo[*b*]fluorenones **38** and **39**, the benzo[*a*]fluorenones **40** were obtained from the ynones **33**, **35**–**37**, although the former were isolated as the major products (Table 1). Interestingly, in the cyclization of **34**, with an *o*-methoxy substituent, the benzo[*a*]fluorenone **40b** was isolated as the major product under method A (Table 1, Entries 4 and 6). The desilylated tetracycle **39a**, with the regiochemistry of naturally occurring benzo[*b*]fluorenones, was obtained in 25% yield following conditions B (Table 1, Entry 5). Treatment of the ynones **33**–**37** with Lewis acids such as $ZnCl_2$ or $Y(OTf)_3$ eed only to unchanged starting materials.

The remarkable formation of benzo[*a*]fluorenones in the cyclization of the ynones **33**–**37** unveils a new rearrangement. A similar rearrangement was subsequently discovered by Saá and co-workers.[28c] A rationale for this transformation was proposed by this group on the basis of the electrocyclization of the initial product, a strained allene **41** to give **42a**,[29] which is in equilibrium with **42b**. Intermediate **42b** then undergoes electrocyclization to form **43** (Scheme 8). An alternative mechanistic suggestion advanced in our pre-

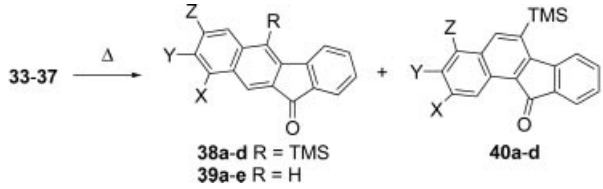


Scheme 6.



Scheme 7.

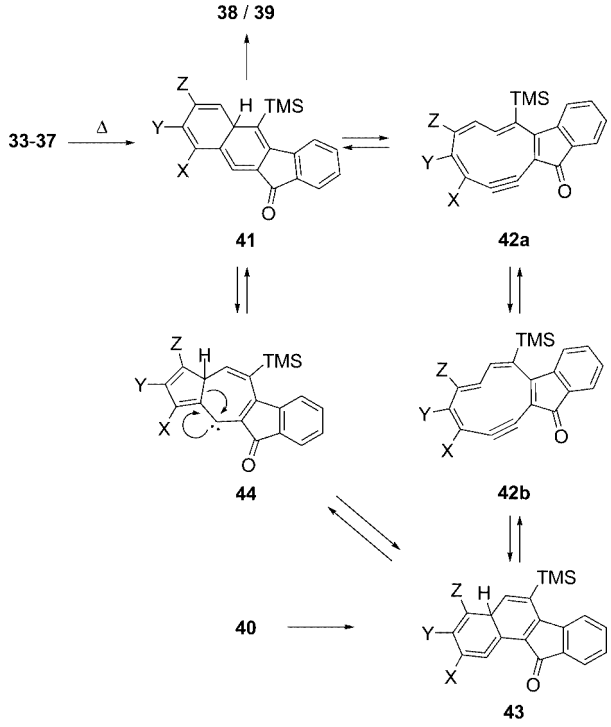
Table 1. Thermal cyclization of arylynones **33**–**37**.



Entry	Ynone	Method[a]	Time [h]	Products (%)[b]	Ratio **38**+**39**/**40**
1	**33**	A	96	**38a** (25), **39a** (18), **40a** (8)	5.3:1
2	**33**	B	14	**38a** (20), **39a** (32), **40a** (24)	2.2:1
3	**33**	C	79	**38a** (11), **39a** (37), **40a** (18)	2.7:1
4	**34**	A	48	**38b** (17)[c], **40b** (63)	1.3.7
5	**34**	B	24	**39b** (25), **40b** (25)	1:1
6	**34**	C	16	**38b** (9)[d], **40b** (30),	1:3.3
7	**35**	A	216	**38c** (13), **39c** (45), **40c** (38)	1.5:1
8	**36**	A	48	**38d** (30), **39d** (9), **40d** (8)	4.9:1
9	**37**	A	48	**38e** (41), **39e** (7), **40e** (14)	3.4:1

[a] A = 1,2-dichlorobenzene under reflux (180 °C); B = celite, 180 °C; C = toluene, γ-terpinene, 180 °C, sealed tube. [b] Isolated yields. [c] Based on 71% conversion. [d] Based on 79% conversion.

liminary communication[27] via intermediates of type **44** seems less likely according to the calculations.[29,36]



Scheme 8.

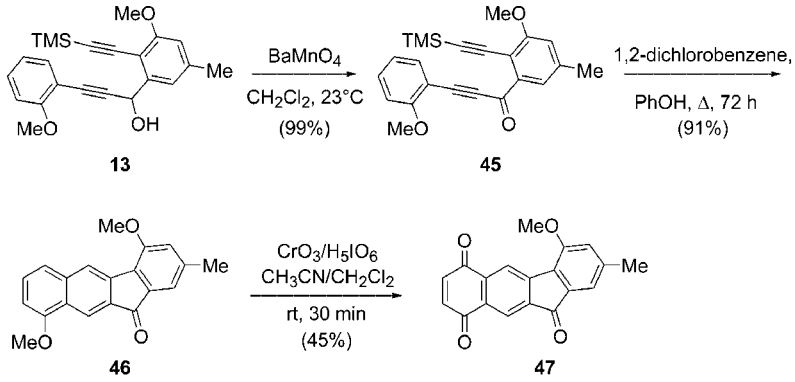
The ynone **45**, with the substitution at the aryl rings required for the synthesis of **3**, was synthesized in 99% yield from the alcohol **13** by oxidation with $BaMnO_4$ (Scheme 9). After some optimization, we found that when the cyclization of **45** was carried out by heating in 1,2-dichlorobenzene under reflux in the presence of phenol (10 equiv.), the desilylated tetracycle **46** was obtained in 91% yield. It is interesting to remark that in the presence of phenol no benzo[*a*]-fluorenone is observed, which suggest that protonation of intermediates of type **41** (Scheme 8) is faster than their equilibration via **42a**–**b**.

Oxidation of the B ring in the tetracyclic **46** was tried under a variety of conditions without success. When the reaction was carried out in a mixture of CH_3CN and CH_2Cl_2 at room temperature for 30 min with H_5IO_6 and CrO_3 as catalyst, the oxidation on the A ring occurred selectively and leads to the quinone **47** as an orange solid in 45% yield (Scheme 9).

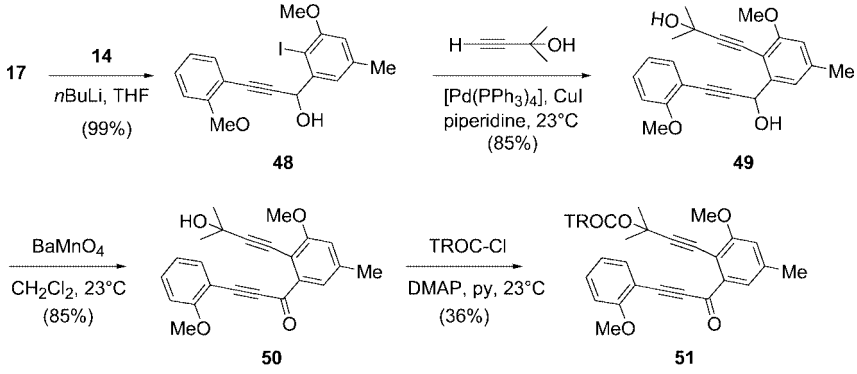
The lithiation of **46** at C-10 assisted by the OMe and carbonyl group using LDA, followed by borylation with $B(OMe)_3$, and reaction with H_2O_2 was also attempted. Unfortunately, after treatment of **46** with LDA, only starting material was recovered.

As all attempts to oxidize the B ring failed, we thought to replace the TMS group by another substituent that could be later transformed into a phenol, thus facilitating the oxidation at the B ring. Thus, we decided to introduce a hydroxyisopropyl group (Me_2COH), which could be converted into a phenol group by the benzylic hydroperoxide rearrangement.[37,38] The preparation of the required substrate began with the reaction between the aldehyde **17** and the lithium acetylide of **14** to give the alcohol **48** in 99% yield (Scheme 10). Sonogashira reaction of **48** with 2-methylbut-3-yn-2-ol afforded **49** (85% yield), which was oxidized with $BaMnO_4$ to give **50**. Protection of the tertiary alcohol as a TROC carbonate proceeded only in poor yield to give **51**.

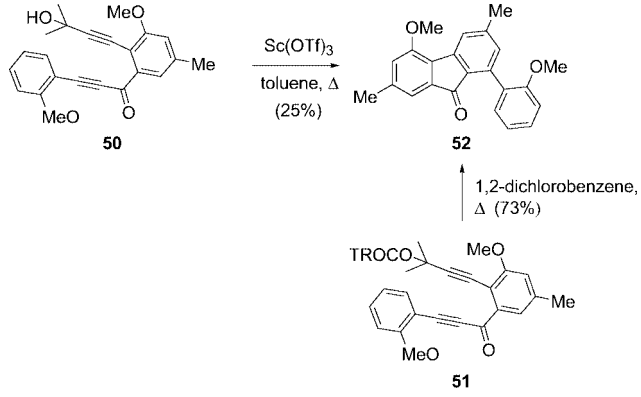
Several attempts to cyclize the ketone **50** were carried out under different reaction conditions, where in most cases very complex mixtures were obtained. On the other hand, heating of compound **50** in toluene with $Sc(OTf)_3$ led to the 9*H*-fluoren-9-one **52** in 25% yield (Scheme 11). Cyclization of the TROC derivative **51** in 1,2-dichlorobenzene in the presence of phenol gave also **52** in 59% yield. The cyclization of **51** actually proceeded more efficiently in the absence of phenol, leading to **52** in 73% yield.



Scheme 9.



Scheme 10.

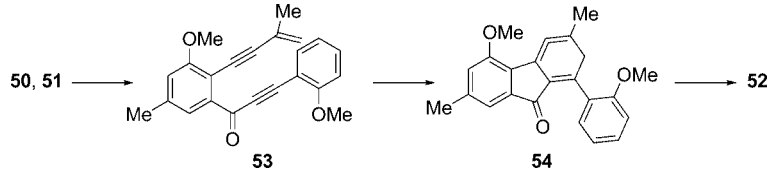


Scheme 11.

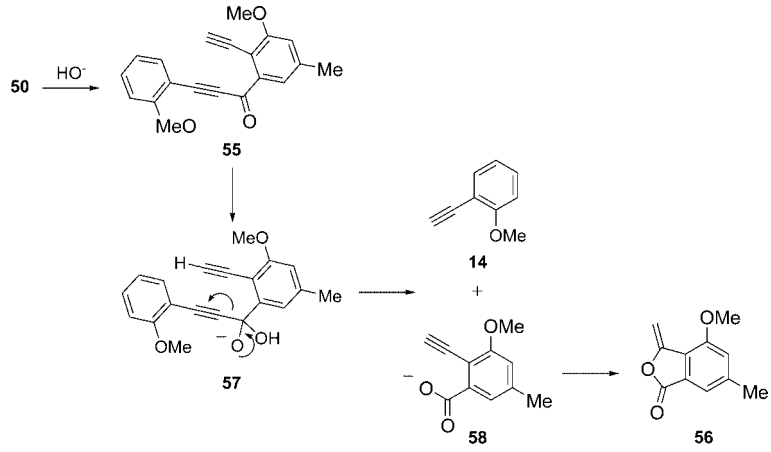
A probable mechanism for the formation of **52** is shown in Scheme 12. Accordingly, the dehydration of **50** could form the 1,3-enyne **53**, which would form the strained six-membered ring allene **54**, which finally gives the 9*H*-fluoren-9-one **52** by a formal 1,5-hydrogen migration.

The elimination of acetone from **50** would afford **55**, which could then be functionalized at the terminal alkyne group with a OTIPS group, whose hydrolysis would allow the direct introduction of the desired phenol at the B ring. However, upon treatment of **50** with NaOH in refluxing toluene for 2 h, a mixture of the alkyne **14** (42%) and the phthalide **56** (25%)[39] was obtained (Scheme 13). Presumably, under the basic conditions, a fragmentation of **55** occurs via the tetrahedral intermediate **57** which yields **14** and the carboxylate **58**, that cyclizes to give the phthalide **56**.

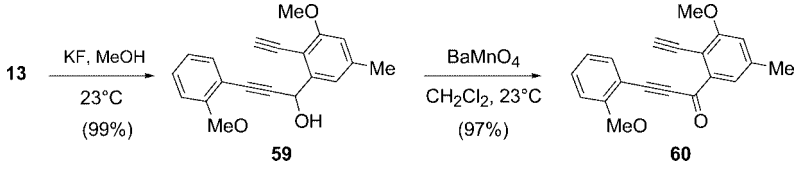
The terminal alkyne **59** was obtained by the deprotection of **13** with KF/MeOH[40] at room temperature in 99% yield (Scheme 14). Oxidation of the alcohol was then carried out with $BaMnO_4$ in CH_2Cl_2 at room temperature to give the ketone **60** in 97% yield. The oxidation of the terminal alkyne of **60** with lithium *tert*-butylperoxide[41] followed by the treatment with triisopropylsilyl trifluoromethanesulfon-



Scheme 12.



Scheme 13.



Scheme 14.

ate[42] led in all cases to mixtures of products. The deprotonation of alkyne with *t*BuLi or *n*BuLi, followed by oxidation with *t*BuOOLi, and treatment with TfOTIPS also failed to provide the desired OTIPS derivative.

Summary

Arylalkyne—allene and arylalkyne–alkyne cycloadditions produce the ready assemblage of the tetracyclic core of the kinamycins. However, all attempts to selectively oxidize the B ring of the resulting aromatized cycloadducts to a quinone to provide the desired compounds failed. We found a rearrangement in the arylalkyne–alkyne cycloadditions that gives rise to benzo[*a*]fluorenones, in addition to the expected benzo[*b*]fluorenones. This rearrangement could be suppressed in the presence of phenol, which allowed to synthesize of 4,9-dimethoxy-2-methyl-11*H*-benzo[*b*]fluoren-11-one (**46**) in excellent yield. Oxidation of **46**, with the substitution pattern of prekinamycin (**3**) and related natural products, led to 4-methoxy-2-methyl-6*H*-benzo[*b*]fluorene-6,9,11-trione (**47**) in moderate yield. On the other hand, 5-methoxy-1-(2-methoxyphenyl)-3,7-dimethyl-9*H*-fluoren-9-one (**52**) was obtained as a result of a 1,3-enyne/alkyne cycloaddition. Work on alternative strategies for the synthesis of members of this family of natural occurring quinonoid compounds are currently underway in our group.

Experimental Section

General Remarks: The NMR spectra were carried out at 23 °C, unless otherwise stated. Only the most significant MS fragmentations are given. The FAB-MS spectra were obtained by using *m*-nitrobenzyl alcohol as the matrix. R_f values were determined on TLC aluminum sheets coated with 0.2 mm GF_{254} silica gel. All reactions were carried out under Ar. Solvents were purified and dried by standard methods. Chromatographic purifications were carried out with flash-grade silica gel. TIPS = triisopropylsilyl, TROC = trichloroethoxycarbonyl.

1-Ethynyl-2-methoxybenzene (14): This acetylene is commercially available (Aldrich). Alternatively, the acetylene **14** was prepared in two steps: (i) To a mixture of 2-iodoanisole (3.600 g, 2.0 mL, 15.38 mmol), $[Pd(PPh_3)_4]$ (440 mg, 0.40 mmol) and CuI (292 mg, 1.54 mmol) in piperidine (50 mL) was added (trimethylsilyl)acetylene (1.580 g, 2.28 mL, 16.15 mmol), and the mixture was stirred at 23 °C for 24 h. The mixture was portioned between Et_2O and a saturated aqueous NH_4Cl (pH 8 with NH_4OH) solution, the organic extract was washed with a 3.5% aqueous HCl solution, followed by a saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 100:1) to give **[2-(methoxyphenyl)ethynyl]trimethylsilane** (3.070 g, 98%) as a colorless oil. R_f = 0.37 (hexane/EtOAc, 100:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.29 (s, 9 H), 3.86 (s, 3 H), 6.85 (d, J = 7.5 Hz, 1 H), 6.89 (td, J = 7.6, 1.0 Hz, 1 H), 7.27 (ddd, J = 7.4, 4.9, 1.7 Hz, 1 H), 7.45 (dd, J = 7.5, 1.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.3 (3 C), 55.6, 98.2, 101.2, 110.5, 112.2, 120.2, 129.9, 134.0, 160.2 ppm. (ii) A mixture of [(methoxyphenyl)ethynyl]trimethylsilane (3.070 g, 15.02 mmol), K_2CO_3 (207 mg, 1.50 mmol) in MeOH (20 mL) was stirred at 23 °C for 20 h. The mixture was portioned between Et_2O and a saturated aqueous NaCl solution, dried ($MgSO_4$) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 125:1) to give **14** (1.804 g, 83%) as a yellow oil. R_f = 0.40 (hexane/EtOAc, 125:1). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.34 (s, 1 H), 3.84 (s, 3 H), 6.84 (dd, J = 8.4, 0.8 Hz, 1 H), 6.89 (ddd, J = 7.6, 7.4, 1.1 Hz, 1 H), 7.28 (ddd, J = 8.4, 7.6, 1.8 Hz, 1 H), 7.46 (dd, J = 7.5, 1.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.4, 79.9, 81.03, 110.3, 110.9, 120.1, 130.0, 133.8, 160.3 ppm.

2-Iodo-3-methoxy-5-methylbenzaldehyde (17): To a solution of *N*,*N*,*N*′-trimethylethylenediamine (747 mg, 0.95 mL, 7.34 mmol) in

THF (15 mL) at –20 °C, was added *n*BuLi (3.1 mL, 2.24 M in hexanes 7.00 mmol). After 5 min aldehyde **16** (1.000 g, 6.67 mmol) was added in THF (15 mL). After 10 min, *n*BuLi (8.9 mL, 2.24 M in hexane, 20.00 mmol) was added and the mixture was stirred at –20 °C for 10 h. After being cooled to –78 °C, 1,2-diiodoethane (4.700 g, 16.68 mmol) in THF (20 mL) was added and the resulting mixture was warmed to 23 °C for 12 h. After being partitioned between Et_2O and a saturated aqueous NaCl solution, the organic extract was dried ($MgSO_4$) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 10:1) to give **17** (1.007 g, 55%) as a white solid. M.p. 74–75 °C. R_f = 0.39 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2956, 2929, 2846, 2739, 1687, 1580, 1384, 1083, 513 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.93 (s, 3 H), 6.87 (br. s, 1 H), 7.32 (br. s, 1 H), 10.16 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.1, 56.7, 117.2, 122.1, 122.9, 136.2, 140.0, 158.1, 196.6 ppm. EI-MS: *m*/*z* (%) = 276 (100) [M^+], 232 (6), 147 (14), 118 (13), 90 (29). $C_9H_9IO_2$ (275.96): calcd. C 39.14, H 3.29; found C 38.83, H 3.44.

3-Methoxy-5-methyl-2-[(trimethylsilyl)ethynyl]benzaldehyde (15): A mixture of **17** (970 mg, 3.52 mmol), (trimethylsilyl)acetylene (518 mg, 0.75 mL, 5.28 mmol), $Pd(OAc)_2$ (40 mg, 0.18 mmol) and PPh_3 (92 mg, 0.36 mmol) in NEt_3 (10 mL) was heated at 80 °C for 20 h. After being cooled to room temperature, the mixture was portioned between EtOAc and a saturated aqueous NaCl solution, the organic extract was dried ($MgSO_4$) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 12:1) to give **15** (710 mg, 82%) as a white solid. M.p. 83–84 °C: R_f = 0.38 (hexane/EtOAc, 9:1). IR (KBr): $\tilde{\nu}$ = 2957, 2839, 2741, 1690, 1584, 1450, 1083, 855 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 2.31 (s, 3 H), 3.83 (s, 3 H), 6.83 (br. s, 1 H), 7.23 (br. s, 1 H), 10.46 (s, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.2 (3 C), 21.6, 56.0, 96.2, 105.8, 113.2, 116.5, 119.0, 137.0, 140.1, 160.7, 191.1 ppm. EI-MS: *m*/*z* (%) = 246 (28) [M^+], 231 (100), 216 (14), 188 (18), 173 (25). $C_{14}H_{18}O_2Si$ (246.11): calcd. C 68.25, H 7.36; found C 67.89, H 7.45.

1-{3-Methoxy-5-methyl-2-[(trimethylsilyl)ethynyl]phenyl}-3-(2-methoxyphenyl)prop-2-yn-1-ol (13): To a solution of **14** (174 mg, 1.32 mmol) in THF (4 mL) at 0 °C was slowly added *n*BuLi (0.55 mL, 2.38 M in hexanes, 1.32 mmol). After 10 min, the aldehyde **15** (324 mg, 1.32 mmol) in THF (4 mL) at 0 °C was added. Then the mixture was warmed to 23 °C and stirred at this temperature for 5 h. The mixture was portioned between EtOAc and a saturated aqueous NaCl solution, the organic extract was dried (Na_2SO_4) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 4:1) to give **13** (412 mg, 83%) as a yellowish-white solid. M.p. 114–115 °C. R_f = 0.22 (hexane/EtOAc, 5:1). IR (KBr): $\tilde{\nu}$ = 3514, 2962, 2833, 2152, 1606, 1495, 1298 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.29 (s, 9 H), 2.38 (s, 3 H), 3.21 (d, *J* = 5.7 Hz, 1 H), 3.87 (s, 6 H), 6.08 (d, *J* = 5.7 Hz, 1 H), 6.66 (br. s, 1 H), 6.85–6.92 (m, 2 H), 7.27–7.31 (m, 2 H), 7.45 (dd, *J* = 4.5, 1.7 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.1 (3 C), 22.0, 55.6, 55.9, 63.8, 82.7, 92.1, 98.8, 104.2, 107.5, 110.5, 111.3, 111.7, 120.0, 120.2, 129.8, 133.7, 140.4, 144.6, 160.1, 160.5 ppm. EI-MS: *m*/*z* (%) = 378 (9) [M^+], 363 (100), 305 (19), 231 (45). $C_{23}H_{26}O_3Si$ (378.17): calcd. C 72.98, H 6.92; found C 72.98, H 6.86.

1-{3-Methoxy-5-methyl-2-[2-(trimethylsilyl)ethynyl]phenyl}-3-(2-methoxyphenyl)prop-2-ynyl Acetate (18): To a mixture of **13** (50 mg, 0.09 mmol) in toluene (2 mL) was added HOAc (0.2 mL), and the reaction was heated under reflux for 16 h. The mixture was cooled to room temperature and was portioned between CH_2Cl_2 and water, the organic extract was dried ($MgSO_4$) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 6:1) to give **18** as a yellow solid (28 mg, 75%). M.p. 91–92 °C. R_f = 0.21 (hexane/EtOAc, 6:1). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.20 (s, 9 H), 2.10 (s, 3 H), 2.41 (s, 3 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 6.71 (s, 1 H), 6.87 (d, *J* = 8.3 Hz, 1 H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.00 (s, 1 H), 7.30 (dd, *J* = 7.5, 1.8 Hz, 1 H), 7.45–7.48 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = –0.10 (3 CH_3), 20.85 (CH_3), 22.16 (CH_3), 55.69 (CH_3), 55.99 (CH_3), 64.70 (CH), 83.59 (C), 89.17 (C), 97.66 (C), 104.10 (C), 109.17 (C), 110.57 (CH), 111.49 (C), 111.97 (CH), 120.28 (CH), 121.48 (CH), 130.15 (CH), 133.88 (CH), 140.03 (C), 140.15 (C), 160.45 (C), 160.53 (C), 169.37 (C) ppm. EI-MS: *m*/*z* (%) = 420 (3) [M^+], 377 (100). EI-HRMS: *m*/*z* for $C_{25}H_{28}O_3Si$ (404.18): calcd. 420.1756; found 420.1730.

10-Chloro-4,9-dimethoxy-2-methyl-11*H*-benzo[*b*]fluorene (21): To a mixture of **13** (100 mg, 0.18 mmol) in anhydrous Et_2O (6 mL) at 0 °C was added a mixture of thionyl chloride (0.01 mL, 0.20 mmol) and pyridine (0.03 mL, 0.39 mmol) in anhydrous Et_2O (4 mL). Then, the reaction mixture was warmed to room temperature. After 16 h water was added, and the mixture was extracted with Et_2O. The combined organic extracts were washed with a saturated NaCl solution, and water, dried (Na_2SO_4), and evaporated to give a yellow oil. This crude oil was heated in toluene (3 mL) under reflux. After 16 h the mixture was cooled to room temperature and concentrated. The mixture was chromatographed (hexane/CH_2Cl_2, 10:1) to give **21** as a yellow solid (16 mg, 24%), along with traces of the 5-TMS compound as shown in the MS. M.p. 169–170 °C. R_f = 0.24 (hexane/CH_2Cl_2, 10:1). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.46 (s, 3 H), 3.99 (s, 3 H), 4.04 (s, 2 H), 4.05 (s, 3 H), 6.73 (s, 1 H), 6.90 (dd, *J* = 6.7, 0.9 Hz, 1 H), 7.01 (s, 1 H), 7.37 (t, *J* = 7.9 Hz, 1 H), 7.54 (dd, *J* = 7.5, 0.8 Hz, 1 H), 8.32 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 22.04 (CH_3), 38.04 (CH_2), 55.32 (CH_3), 56.17 (CH_3), 106.95 (CH), 109.88 (CH), 118.08 (CH), 120.37 (CH), 120.98 (C), 122.03 (CH), 124.74 (C), 125.65 (CH), 126.30 (C), 137.56 (C), 139.50 (C), 139.58 (C), 140.74 (C), 145.33 (C), 156.32 (C), 156.47 (C) ppm. EI-MS: *m*/*z* (%) = 396 (3) [M^+ + TMS], 324 (100) [M^+], 289 (55) [M^+ – Cl]. EI-HRMS: *m*/*z* for $C_{23}H_{25}ClO_2Si$: calcd. 396.1312; found 396.1316; calcd. for $C_{20}H_{17}ClO_2$: 324.0917, found 324.0913.

3-Phenyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-ol (23): To a solution of phenylacetylene (630 mg, 3.12 mmol) in THF (20 mL) at 0 °C was added *n*BuLi (1.25 mL, 2.5 M solution in hexanes, 3.12 mmol). After 30 min, 2-[2-(trimethylsilyl)ethynyl]benzaldehyde (**22**)[33] (318 mg, 3.12 mmol) in THF (20 mL) was added, and the mixture was stirred for 5 h at 23 °C. The mixture was diluted with EtOAc, washed with a saturated NaCl solution, and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 10:1) to give **23** as a yellow oil (757 mg, 80%). R_f = 0.32 (hexane/EtOAc, 10:1). ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.30 (s, 9 H), 3.11 (br. s, 1 H), 6.08 (d, *J* = 5.5 Hz, 1 H), 7.26–7.34 (m, 4 H), 7.38 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.47–7.54 (m, 3 H), 7.74 (dd, *J* = 7.9, 1.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = –0.13 (3 CH_3), 63.74 (CH), 86.43 (C), 88.14 (C), 100.71 (C), 102.35 (C), 121.16 (CH), 122.55 (CH), 126.68 (CH), 128.12 (CH), 128.23 (CH), 128.49 (CH), 129.14 (CH), 131.77 (3 CH), 132.78 (CH), 142.87 (C) ppm. EI-MS: *m*/*z* (%) = 304 (3) [M^+], 288 (13), 213 (34). EI-HRMS: *m*/*z* for $C_{20}H_{20}OSi$: calcd. 304.1283; found 304.1288. $C_{20}H_{20}OSi$ (304.13): calcd. C 78.90, H 6.62; found C 78.52, H 7.04.

10-Chloro-11*H*-benzo[*b*]fluorene (24): To a mixture of **23** (100 mg, 0.33 mmol) in anhydrous Et_2O (10 mL) at 0 °C was added a mixture of thionyl chloride (0.03 mL, 0.36 mmol), and pyridine (0.06 mL, 0.73 mmol) in anhydrous Et_2O (5 mL). Then, the reac-

tion mixture was warmed to room temperature. After 16 h water was added, and the mixture was extracted with Et_2O. The combined organic extracts were washed with a saturated NaCl solution, and water, dried (Na_2SO_4), and evaporated to give a yellow oil. This crude oil was heated in xylene (5 mL) under reflux for 16 h. The mixture was cooled to room temperature, and evaporated and the residue was chromatographed (hexane) to give **24** as a white solid (24 mg, 29%). M.p. 106–107 °C. R_f = 0.55 (hexane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.13 (s, 2 H), 7.36–7.46 (m, 2 H), 7.51–7.62 (m, 3 H), 7.90–7.97 (m, 2 H), 8.12 (s, 1 H), 8.31 (dd, J = 8.9, 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 36.83 (CH_2), 116.87 (CH), 120.80 (CH), 123.82 (CH), 125.31 (CH), 126.09 (CH), 126.33 (CH), 127.12 (CH), 127.59 (C), 127.99 (CH), 128.44 (CH), 130.03 (C), 134.37 (C), 139.28 (C), 140.59 (C), 140.73 (C), 142.97 (C) ppm. EI-MS: m/z (%) = 250 (11) [M$^+$], 215 (100). EI-HRMS: m/z for $C_{17}H_{11}Cl$: calcd. 250.0549; found 250.0553.

Diphenyl[3-(5-methyl-3-methoxy-2-trimethylsilylethynylphenyl)-1-(2-methoxyphenyl)-1,2-propadienyl]oxophosphorane (25): To a solution of **13** in THF (10 mL) at –78 °C was added NEt_3 (184 mg, 0.25 mL, 1.82 mmol) and Ph_2PCl (387 mg, 0.32 mL, 1.75 mmol). The mixture was warmed to –40 °C for 30 min, and the resulting solution was stirred for 90 min at this temperature. The mixture was portioned between EtOAc and a saturated NaCl solution, the organic extract was dried (Na_2SO_4) and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 1:1) to give **25** (731 mg, 93%) as a vitreous yellow solid. R_f = 0.21 (hexane/EtOAc, 1:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3056, 2919, 2222, 2144, 1931, 1567, 1470, 1074, 872. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 9 H), 2.31 (s, 3 H), 3.61 (s, 3 H), 3.80 (s, 3 H), 6.48 (br. s, 1 H), 6.74 [d, J (^{1}H-^{31}P) = 11 Hz, 1 H], 6.83 (br. s, 1 H), 6.89 (td, J = 7.6, 1.0 Hz, 1 H), 7.20 (td, J = 7.7, 1.7 Hz, 1 H), 7.25–7.49 (m, 7 H), 7.64 (dt, J = 7.6, 1.4 Hz, 1 H), 7.74–7.86 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.04 (3 C), 21.95, 55.19, 55.78, 94.01, 94.20, 98.98, 99.62, 100.93, 103.27, 107.87, 109.96, 111.13, 119.86, 120.78, 127.80 [d, J (^{13}C-^{31}P) = 6.3 Hz], 127.97 [d, J (^{13}C-^{31}P) = 6.3 Hz], 130.63, 129.23, 131.58–131.38 (m, 2 C), 132.01 [d, J (^{13}C-^{31}P) = 6.3 Hz], 133.40 [d, J (^{13}C-^{31}P) = 6.3 Hz], 135.68 [d, J (^{13}C-^{31}P) = 8.4 Hz], 139.05, 156.70, 156.76, 160.38, 214.27 ppm. EI-MS: m/z = 562 (100) [M$^+$], 531 (46), 490 (57), 361 (70). $C_{35}H_{35}O_3PSi$ (562.21): calcd. C 74.71, H 6.27; found C 74.33, H 6.34.

Diphenyl[10-(4,9-dimethoxy-2-methyl-5-(trimethylsilyl)-11*H*-benzo[*b*]fluorenyl)]oxophosphorane (26): A solution of **25** (180 mg, 0.32 mmol) and 1,4-cyclohexadiene (0.45 mL, 4.8 mmol) in toluene (9 mL) was heated at 110 °C for 48 h. The solvent was evaporated and the residue was chromatographed (hexane/EtOAc, 1:1) to give **26** (105 mg, 58%) as a pale red solid. M.p. 111–112 °C. R_f = 0.20 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3055, 2934, 1608, 1555, 1458, 1263, 1088. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 9 H), 2.40 (s, 3 H), 2.82 (s, 3 H), 3.90 (s, 3 H), 4.40–4.20 (m, 2 H), 6.40 (d, J = 7.7 Hz, 1 H), 6.61 (br. s, 1 H), 6.88 (br. s, 1 H), 7.33 (t, J = 8.1 Hz, 1 H), 7.31–7.44 (m, 6 H), 7.62–7.74 (m, 4 H), 7.83 (dd, J = 8.0, 1.4 Hz, 1 H) PPM. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 2.30 (3 C), 21.90, 38.97, 52.57, 54.38, 104.56, 109.27, 117.72, 118.18, 119.55, 121.51, 123.62 [d, J (^{13}C-^{31}P) = 6.0 Hz], 124.52, 127.70, 127.94, 128.10, 130.44, 138.06, 139.90 [d, J (^{13}C-^{31}P) = 6.4 Hz], 140.13, 147.06, 147.17, 151.36 [d, J (^{13}C-^{31}P) = 6.2 Hz], 153.91, 154.56 ppm (4 signals were missing due to poor relaxation or overlapping). EI-MS m/z (%) = 562 (100) [M$^+$], 490 (16), 439 (8), 361 (6). EI-HRMS: m/z for $C_{35}H_{35}O_3PSi$: calcd. 562.2093; found: 562.2083.

3-(2-Methoxyphenyl)-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-ol (29): *n*BuLi (0.39 mL 2.5 M in hexanes) was slowly added to a solution of 2-ethynylanisole (**14**) (129 mg, 0.98 mmol) in THF (4 mL) at 0 °C. After stirring for 30 min, a solution of **22** (200 mg, 0.98 mmol) in THF (4 mL) was added. The reaction mixture was stirred at 23 °C for 5 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 30:1) to give **29** as a yellow oil (235 mg, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.27 (s, 9 H), 3.30 (br. s, 1 H, OH), 3.81 (s, 3 H), 6.15 (s, 1 H), 6.83 (d, J = 8.5 Hz, 1 H), 6.88 (td, J = 8.5, 0.8 Hz, 1 H), 7.29–7.22 (m, 2 H), 7.34 (td, J = 7.3, 1.2 Hz, 1 H), 7.42 (dd, J = 7.3, 1.6 Hz, 1 H), 7.49 (dd, J = 7.7, 1.6 Hz, 1 H), 7.84 (dd, J = 8.1, 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.27 (3 CH_3), 55.55 (CH_3), 63.50 (CH), 82.72 (C), 92.23 (C), 100.12 (C), 102.32 (C), 110.49 (C), 111.61 (C), 120.20 (CH), 121.20 (CH), 126.81 (CH), 127.87 (CH), 128.93 (CH), 129.82 (CH), 132.44 (CH), 133.56 (CH), 142.87 (C), 159.97 (C) ppm.

3-*o*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-ol (30): *n*BuLi (0.61 mL 2.5 M in hexanes) was slowly added to a solution of 2-ethynyltoluene (178 mg, 1.53 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, a solution of **22** (310 mg, 1.53 mmol) in THF (5 mL) was added. The reaction mixture was stirred at 23 °C for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 7:1) to give **30** as a yellow oil (373.5 mg, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.37 (s, 9 H), 2.51 (s, 3 H), 3.40 (br. s, 1 H, OH), 6.22 (s, 1 H), 7.26–7.23 (m, 1 H), 7.25–7.30(m, 2 H), 7.33 (td, J = 7.7, 1.6 Hz, 1 H), 7.43 (td, J = 7.7, 1.6 Hz, 1 H), 7.52 (br. d, J = 7.3 Hz, 1 H), 7.59 (dd, J = 7.3, 1.2 Hz, 1 H), 7.83 (dd, J = 7.7, 1.2 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.28 (3 CH_3), 20.55 (CH_3), 63.52 (CH), 85.14 (C), 92.12 (C), 100.37 (C), 102.37 (C), 120.89 (C), 122.18 (C), 125.31 (CH), 126.39 (CH), 127.84 (CH), 128.32 (CH), 128.96 (CH), 129.21 (CH), 131.94 (CH), 132.61 (CH), 140.14 (C), 143.04 (C) ppm. $C_{21}H_{22}OSi$ (318.14): calcd. C 79.20, H 6.96; found C 78.78, H 7.39.

3-*m*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-ol (31): *n*BuLi (0.5 mL 2.5 M in hexanes) was slowly added to a solution of 3-ethynyltoluene (188 mg, 1.61 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, a solution of **22** (325 mg, 1.53 mmol) in THF (5 mL) was added. The reaction mixture was stirred at 23 °C for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 7:1) to give **31** as a yellow oil (249 mg, 49%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.32 (s, 9 H), 2.32 (s, 3 H), 3.21 (s, 1 H, OH), 6.09 (s, 1 H), 7.14 (br. d, J = 7.3 Hz, 1 H), 7.21 (br. t, J = 7.6 Hz, 1 H), 7.27–7.31 (m, 3 H), 7.39 (br. d, J = 7.3 Hz, 1 H), 7.53 (br. d, J = 7.3 Hz, 1 H), 7.76 (br. d, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.23 (3 CH_3), 21.03 (CH_3), 63.58 (CH), 86.45 (C), 87.79 (C), 100.51 (C), 102.32 (C), 121.04 (C), 122.26 (C), 126.11 (CH), 127.95 (CH), 128.01 (CH), 128.70 (CH), 129.01 (CH), 129.24 (CH), 132.25 (CH), 132.64 (CH), 137.74 (C), 142.90 (C) ppm. $C_{21}H_{22}OSi$ (318.14): calcd. C 79.20, H 6.96; found C 78.63, H 7.41.

3-*p*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-ol (32): *n*BuLi (0.54 mL 2.5 M in hexanes) was slowly added to a solution of 4-ethynyltoluene (157 mg, 1.35 mmol) in THF (10 mL) at 0 °C. After stirring for 30 min, a solution of **22** (273 mg, 1.31 mmol) in THF (10 mL) was added. The reaction mixture was stirred at 23 °C for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent

was evaporated, and the residue was chromatographed (hexane/EtOAc, 7:1) to give **32** as a yellow oil (230 mg, 54%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.28 (s, 9 H), 2.35 (s, 3 H), 2.91 (d, J = 5.4 Hz, 1 H, OH), 6.05 (d, J = 5.4 Hz, 1 H), 7.12 (br. d, J = 7.5 Hz, 1 H), 7.25–7.43 (m, 5 H), 7.52 (br. d, J = 7.5 Hz, 1 H), 7.74 (br. d, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT): δ = –0.28 (3 CH_3), 21.21 (CH_3), 63.41 (CH), 86.25 (C), 87.44 (C), 100.35 (C), 102.33 (C), 119.31 (C), 120.89 (C), 126.41 (CH), 127.77 (CH), 128.73 (CH), 128.89 (CH), 131.43 (CH), 132.45 (CH), 138.26 (C), 142.88 (C) ppm. $C_{21}H_{22}OSi$ (318.14): calcd. C 79.20, H 6.96; found C 78.69, H 7.13.

3-Phenyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (33): $BaMnO_4$ (343 mg, 1.34 mmol) was added to a solution of **23** (203 mg, 0.67 mmol) in CH_2Cl_2 (20 mL) at 23 °C. The reaction mixture was stirred for 3 days, filtered through celite and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 9:1) to give **33** as a yellow oil (184 mg, 91%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.21 (s, 9 H), 7.36–7.55 (m, 5 H), 7.59–7.72 (m, 3 H), 8.10 (dd, J = 7.9, 1.9 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.26 (3 CH_3), 87.97 (C), 93.30 (C), 101.36 (C), 102.90 (C), 120.18 (C), 122.60 (C), 128.24 (CH), 128.61 (CH), 130.77 (CH), 131.19 (CH), 132.27 (CH), 133.14 (CH), 134.99 (CH), 138.88 (CH), 177.48 (C) ppm. $C_{20}H_{18}OSi$ (302.11): calcd. C 79.43, H 6.00; found C 79.15, H 6.12.

3-(2-Methoxyphenyl)-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (34): $BaMnO_4$ (1.501 g, 5.86 mmol) was added to a solution of **29** (980 mg, 2.93 mmol) in CH_2Cl_2 (20 mL) at 23 °C. The reaction mixture was stirred for 3 days, filtered through celite and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 8:1) to give **34** as a yellow solid (774 mg, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.22 (s, 9 H), 3.93 (s, 3 H), 6.91–6.99 (m, 2 H), 7.39–7.51 (m, 3 H), 7.56–7.62 (m, 2 H), 8.29–8.33 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = –0.25 (3 CH_3), 55.83 (CH_3), 90.30 (C), 92.00 (C), 100.90 (C), 103.22 (C), 92.00 (C), 109.55 (C), 110.83 (CH), 120.59 (CH), 122.57 (C), 128.04 (CH), 132.05 (CH), 132.47 (CH), 134.98 (CH), 138.89 (C), 161.76 (C), 177.21 (C) ppm.

3-*o*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (35): $BaMnO_4$ (395 mg, 1.54 mmol) was added to a solution of **30** (245 mg, 0.77 mmol) in CH_2Cl_2 (15 mL) at 23 °C. The reaction mixture was stirred for 17 h, filtered through celite and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 10:1) to give **35** as a yellow oil (228 mg, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.22 (s, 9 H), 2.51 (s, 3 H), 7.17 (br. t, J = 8 Hz, 1 H), 7.22 (br. d, J = 8 Hz, 1 H), 7.31 (td, J = 7.7, 1.2 Hz, 1 H), 7.41 (td, J = 7.3, 1.2 Hz, 1 H), 7.47 (td, J = 7.7, 1.6 Hz, 1 H), 7.58 (dd, J = 6.5, 1.0 Hz, 1 H), 7.59 (dd, J = 7.3, 2.0 Hz, 1 H), 8.11 (dd, J = 7.7, 1.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.42 (3 CH_3), 20.55 (CH_3), 91.59 (C), 92.20 (C), 101.12 (C), 102.91 (C), 119.78 (C), 122.35 (C), 125.70 (CH), 128.04 (CH), 129.63 (CH), 130.66 (CH), 130.97 (CH), 132.03 (CH), 133.50 (CH), 134.84 (CH), 138.86 (C), 142.04 (C), 177.18 (C) ppm. EI-MS: m/z (%) = 316 (33) [M^+], 301 (100).

3-*m*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (36): $BaMnO_4$ (356 mg, 1.38 mmol) was added to a solution of **31** (221 mg, 0.69 mmol) in CH_2Cl_2 (15 mL) at 23 °C. The reaction mixture was stirred for 17 h, filtered through celite and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 10:1) to give **36** as a yellow solid (182 mg, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.22 (s, 9 H), 2.34 (s, 3 H), 7.25–7.30 (m, 2 H), 7.40–7.50 (m, 4 H), 7.61 (dd, J = 6.9, 1.6 Hz, 1 H), 8.10 (dd, J = 7.7, 1.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.36 (3 CH_3), 21.03 (CH_3), 87.68 (C), 93.59 (C), 101.21 (C), 102.85 (C), 119.89 (C), 122.49 (C), 128.12 (CH), 128.41 (CH), 130.21 (CH), 131.05 (CH), 131.61 (CH), 132.11 (CH), 133.50 (CH), 134.87 (CH), 138.27 (C), 138.86 (C), 177.37 (C) ppm. EI-MS: m/z (%) = 316 (33) [M^+], 301 (100), 242 (19).

3-*p*-Tolyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}prop-2-yn-1-one (37): $BaMnO_4$ (369 mg, 1.44 mmol) was added to a solution of **32** (230 mg, 0.72 mmol) in CH_2Cl_2 (20 mL) at 23 °C. The reaction mixture was stirred for 3 days, filtered through celite and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 9:1) to give **37** as a yellow oil (206 mg, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.21 (s, 9 H), 2.39 (3 H), 7.20 (br. d, J = 8.0 Hz, 2 H), 7.43 (td, J = 7.6, 1.5 Hz, 1 H), 7.49 (td, J = 7.4, 1.6 Hz, 1 H), 7.54 (br. d, J = 8.2 Hz, 2 H), 7.61(dd, J = 7.7, 1.6 Hz, 1 H), 8.09 (dd, J = 7.4, 1.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = –0.27 (3 CH_3), 21.74 (CH_3), 87.89 (C), 94.02 (C), 101.25 (C), 102.90 (C), 117.10 (C), 122.55 (C), 128.16 (CH), 129.39 (CH), 131.12 (CH), 132.11 (CH), 133.20 (CH), 134.94 (CH), 139.07 (C), 141.48 (C), 177.61 (C) ppm. $C_{21}H_{20}OSi$ (316.13): calcd. C 79.70, H 6.37; found C 79.38, H 6.16.

Thermal Cyclization of Diaryldiynones in 1,2-Dichlorobenzene. General Procedure: A solution of **33**–**37** in 1,2-dichlorobenzene (0.2 M for **33**, 0.06–0-09 M for **34**–**37**) was heated under reflux for the stated time (Table 1). The solvent was evaporated, and the residue was chromatographed (gravity column, hexane/EtOAc, 30:1).

2-Methoxy-6-(trimethylsilyl)benzo[*a*]fluorene-11-one (40b): ^{1}H NMR (C_6D_6, 500 MHz): δ = 0.29 (s, 9 H), 3.52 (s, 3 H), 6.81 (t, J = 7.6 Hz, 9-H or 8-H), 7.00 (td, J = 7.6, 1.2 Hz, 8-H or 9-H), 7.09 (dd, J = 9.0, 2.6 Hz, 3-H), 7.33 (d, J = 9.0 Hz, 4-H), 7.63 (d, J = 5.9 Hz, 10-H or 7-H), 7.64 (d, J = 5.9 Hz, 7-H or 10-H), 7.95 (s, 5-H), 8.84 (d, J = 2.5 Hz, 1-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 0.29 (3 CH_3), 55.54 (CH_3), 101.61 (CH, C-1), 116.87 (C), 119.96 (CH), 123.62 (CH), 125.81 (C), 128.63 (CH), 129.20 (C), 129.31 (CH), 130.10 (CH), 132.08 (C), 133.60 (CH), 135.22 (C), 142.70 (CH, C-5), 144.95 (C), 151.40 (C), 161.21 (C), 196.24 (C) ppm. EI-MS: m/z (%) = 332 (98) [M^+], 317 (100), 289 (47). The structure was supported by COSY experiment (C_6D_6, 500 MHz), HMQC and HMBC experiments.

6-(Trimethylsilyl)benzo[*a*]fluorene-11-one (40a): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.55 (s, 9 H), 7.26 (td, J = 7.4, 0.9 Hz, 1 H), 7.40–7.47 (m, 2 H), 7.51–7.62 (m, 1 H), 7.62–7.65 (m, 1 H), 7.67 (d, J = 7.6 Hz, 1 H), 7.77 (br. d, J = 8.2 Hz, 1 H), 8.16 (s, 1 H), 9.06 (dd, J = 8.5, 1.1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 0.66, 123.97, 124.05, 124.62, 126.98, 127.34, 128.85, 129.10, 130.27, 130.68, 132.62, 133.72, 134.11, 135.41, 143.50, 145.47, 151.30, 196.52 ppm. EI-MS: m/z (%) = 302 (100) [M^+], 287 (96), 259 (56).

2-Methyl-6-(trimethylsilyl)benzo[*a*]fluorene-11-one (40c): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.57 (s, 9 H), 2.56 (s, 3 H), 7.25–7.28 (m, 2 H), 7.45 (td, J = 7.6, 1.1 Hz, 1 H), 7.64–7.69 (m, 3 H), 8.12 (s, 1 H), 8.87 (d, J = 0.6, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 0.71 (3 CH_3), 22.64 (CH_3), 123.49 (CH), 123.90 (CH), 123.93 (CH), 126.75 (C), 128.69 (CH), 128.99 (CH), 129.30 (CH), 130.96 (C), 131.36 (C), 132.20 (C), 134.02 (CH), 135.49 (C), 140.70 (C), 143.26 (CH), 145.51 (C), 151.40 (C), 196.60 (C) ppm. EI-MS: m/z (%) = 316 (100) [M^+], 302 (99), 243 (11).

3-Methyl-6-(trimethylsilyl)benzo[*a*]fluorene-11-one (40d): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.56 (s, 9 H), 2.51 (s, 3 H), 7.27 (t, J = 7.4 Hz, 1 H), 7.43–7.46 (m, 2 H), 7.57 (s, 1 H), 7.64 (d, J = 7.2 Hz, 1 H), 7.66 (d, J = 7.6 Hz, 1 H), 8.10 (s, 1 H), 8.96 (d, J = 8.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 0.67 (3 CH_3), 22.12 (CH_3), 113.02 (C), 123.81 (CH), 123.99 (CH), 124.37 (CH), 127.35 (C), 127.76 (CH), 128.88 (CH), 132.53 (C), 132.63 (CH),

134.03 (C), 134.10 (CH), 135.40 (C), 136.75 (C), 142.77 (CH), 145.67 (C), 150.41 (C), 196.67 (C) ppm. EI-MS: *m*/*z* = 316 (100) [M$^+$], 301 (82), 229 (10).

4-Methyl-6-(trimethylsilyl)benzo[*a*]fluorene-11-one (40e): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.56 (s, 9 H), 2.69 (s, 3 H), 7.29–7.24 (m, 3-H and 9-H), 7.43 (td, *J* = 7.6, 1.3 Hz, 8-H), 7.48 (dd, *J* = 8.5, 6.9 Hz, 2-H), 7.63 (dt, *J* = 7.1, 0.6 Hz, 10-H), 7.67 (d, *J* = 7.6 Hz, 7-H), 8.39 (s, 5-H), 8.96 (d, *J* = 8.4 Hz, 1-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 0.17 (3 CH_3), 19.41 (CH_3), 122.40 (CH), 123.43 (CH), 123.54 (CH), 127.11 (C), 127.34 (CH), 128.59 (CH), 129.65 (CH), 130.54 (C), 131.61 (C), 132.33 (C), 133.61 (CH), 134.76 (C), 135.00 (C), 138.91 (CH), 144.85 (C), 150.32 (C), 196.08 (C) ppm. EI-MS: *m*/*z* (%) = 316 (100) [M$^+$], 301 (82), 273 (45). The structure was supported by a NOESY experiment (500 MHz, $CDCl_3$).

9-Methoxy-5-(trimethylsilyl)benzo[*b*]fluorene-11-one (38b): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.60 (s, 9 H), 4.00 (s, 3 H), 6.81 (d, *J* = 7.7 Hz, 1 H), 7.34 (t *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 1 H), 7.52 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.68 (d, *J* = 8.6 Hz, 1 H), 7.76 (d, *J* = 7.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 8.70 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 3.17 (3 CH_3), 55.66 (CH_3), 104.90 (CH), 121.20 (C), (one carbon signal was not observed), 122.29 (CH), 124.03 (CH), 124.51 (C), 126.45 (CH), 128.12 (CH), 128.73 (CH), 132.21 (C), 133.56 (CH), 136.77 (C), 142.67 (C), 146.57 (C), 147.57 (C), 157.85 (C), 193.20 (C) ppm. EI-MS: *m*/*z* (%) = 322 (100) [M$^+$], 317 (82), 273 (21).

9-Methyl-5-(trimethylsilyl)benzo[*b*]fluorene-11-one (38c): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.63 (s, 9 H), 2.75 (s, 3 H), 7.31 (d, *J* = 7.0 Hz, 1 H), 7.37 (td, *J* = 7.3, 0.8 Hz, 1 H), 7.42 (dd, *J* = 8.3, 7.0 Hz, 1 H), 7.56 (td, *J* = 7.8, 1.3 Hz, 1 H), 7.79 (d, *J* = 7.8 Hz, 1 H), 7.82 (d, *J* = 7.3 Hz, 1 H), 8.00 (d, *J* = 8.3 Hz, 1 H), 8.43 (d, *J* = 0.8 Hz, 1 H) ppm. EI-MS: *m*/*z* (%) = 316 (89) [M$^+$], 301 (100), 273 (38).

8-Methyl-5-(trimethylsilyl)benzo[*b*]fluorene-11-one (38d): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.61 (s, 9 H), 2.72 (s, 3 H), 7.32 (td, *J* = 7.4, 0.8 Hz, 1 H), 7.35 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.52 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.63 (br. s, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.77 (d, *J* = 8.6 Hz, 1 H), 8.02 (d, *J* = 8.6 Hz, 1 H), 8.09 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 3.62 (3 CH_3), 21.60 (CH_3), 124.54 (CH), 126.60 (CH), 126.81 (CH), 129.01 (CH), 130.14 (CH), 130.39 (CH), 130.80 (CH), 133.36 (C), 133.54 (C), 134.25 (CH), 134.89 (C), 136.57 (CH), 137.03 (C), 140.17 (C), 146.59 (C), 147.32 (C), 193.82 (C) ppm. EI-MS: *m*/*z* (%) = 316 (98) [M$^+$], 301 (100), 273 (52).

7-Methyl-5-(trimethylsilyl)benzo[*b*]fluorene-11-one (38e): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.64 (s, 9 H), 2.55 (s, 3 H), 7.30 (dd, *J* = 8.2, 1.5 Hz, 8-H), 7.36 (td, *J* = 7.5, 0.8 Hz, 2-H), 7.55 (td, *J* = 7.5, 1.3 Hz, 3-H), 7.78–7.81 (m, 1-H, 4-H, 9-H), 7.93 (br. d, *J* = 0.8 Hz, 6-H), 8.15 (s, 10-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 3.36 (3 CH_3), 22.08 (CH_3), 123.99 (CH), 126.39 (CH), 128.20 (CH), 128.65 (CH), 129.57 (CH), 130.66 (C), 130.88 (CH), 132.33 (C), 133.64 (CH), 133.84 (C), 136.68 (C), 137.91 (CH), 141.78 (C), 146.69 (C), 147.08 (C), 193.15 (C) (one carbon signal was not observed); Long range ^{1}H-^{13}C correlations were observed between the carbonyl carbon (δ = 193.15) and 10-H (s, 8.15 ppm) and 1-H (m, 7.81–7.78). The ^{1}H NMR assignment was based on a NOESY experiment (500 MHz, $CDCl_3$). EI-MS: *m*/*z* (%) = 316 (91) [M$^+$], 301 (100), 273 (41).

9-Methoxybenzo[*b*]fluorene-11-one (39b): ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.01 (s, 3 H), 6.83 (dd, *J* = 7.6, 1.0 Hz, 1 H), 7.35 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.39–7.50 (m, 2 H), 7.56 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.70–7.73 (m, 2 H), 7.83 (s, 1 H), 8.67 (s, 1 H) ppm. EI-MS: *m*/*z* (%) = 260 (100) [M$^+$], 217 (75), 189 (28).

Benzo[*b*]fluorene-11-one (39a):[28b,43] ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35 (dt, *J* = 7.4, 0.9 Hz, 1 H), 7.47 (td, *J* = 8.1, 1.2 Hz, 1 H), 7.55 (td, *J* = 8.1, 1.3 Hz, 1 H), 7.56 (td, *J* = 7.4, 1.1 Hz, 1 H), 7.72 (dt, *J* = 7.5, 0.8 Hz, 1 H), 7.75 (dt, *J* = 8.2, 0.7 Hz, 1 H), 7.83 (dd, *J* = 8.1, 0.6 Hz, 1 H), 7.87 (s, 1 H), 7.89 (dt, *J* = 8.1, 0.6 Hz, 1 H), 8.17 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 119.48 (CH), 121.41 (CH), 124.90 (CH), 126.13 (CH), 127.36 (CH), 129.19 (CH), 129.42 (CH), 129.61 (CH), 131.24 (CH), 133.24 (C), 134.08 (C), 135.43 (CH), 136.62 (C), 137.36 (C), 138.84 (C), 145.28 (C), 193.53 (C) ppm. EI-MS: *m*/*z* (%) = 230 (100) [M$^+$], 202 (22).

9-Methylbenzo[*b*]fluorene-11-one (39c): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.74 (s, 3 H), 7.33 (d, *J* = 7.0 Hz, 1 H), 7.37 (td, *J* = 7.5, 0.8 Hz, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.58 (td, *J* = 7.4, 1.0 Hz, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.74 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 7.4 Hz, 1 H), 7.89 (s, 1 H), 8.40 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 30.11 (CH_3), 120.11 (CH), 121.40 (CH), 122.53 (CH), 124.89 (CH), 127.61 (CH), 128.36 (CH), 129.21 (CH), 129.54 (CH), 132.93 (CH), 133.23 (C), 135.39 (CH), 136.68 (C), 137.67 (C), 138.12 (C), 138.51 (C), 145.27 (C), 193.82 (C) ppm. EI-MS: *m*/*z* (%) = 244 (100) [M$^+$], 215 (43).

8-Methylbenzo[*b*]fluorene-11-one (39d): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.50 (s, 3 H), 7.33 (td, *J* = 7.5, 0.9 Hz, 1 H), 7.38 (dd, *J* = 8.4, 1.4 Hz, 1 H), 7.55 (td, *J* = 7.5, 1.1 Hz, 1 H), 7.66 (br. s, 1 H), 7.69 (dd, *J* = 7.5, 0.7 Hz, 1 H), 8.09 (s, 1 H), 7.82 (s, 1 H), 7.74 (dd, *J* = 7.5, 0.7 Hz, 1 H), 7.73 (d, *J* = 8.4 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT): δ = 21.95 (CH_3), 119.30 (CH), 121.25 (CH), 124.85 (CH), 125.60 (CH), 128.97 (CH), 129.36 (CH), 130.46 (CH), 131.59 (CH), 133.29 (C), 134.27 (C), 135.39 (CH), 135.48 (C), 136.55 (C), 137.32 (CH), 138.06 (C), 145.46 (C), 193.74 (C) ppm. EI-MS: *m*/*z* (%) = 244 (100) [M$^+$], 215 (41).

7-Methylbenzo[*b*]fluorene-11-one (39e): ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.52 (s, 3 H), 7.30 (dd, *J* = 8.3, 1.6 Hz, 8-H), 7.34 (td, *J* = 7.4, 1.0 Hz, 3-H), 7.55 (td, *J* = 7.5, 1.2 Hz, 2-H), 7.61 (s, 6-H), 7.71 (dt, *J* = 7.5, 0.9 Hz, 1-H), 7.75 (dt, *J* = 7.4, 0.8 Hz, 9-H), 7.78 (s, 5-H), 7.79 (d, *J* = 8.1 Hz, 4-H), 8.13 (s, 10-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT): δ = 21.84 (CH_3), 118.47 (CH), 120.90 (CH), 124.35 (CH), 125.52 (CH), 128.12 (CH), 129.00 (CH), 130.57 (CH), 131.74 (C), 132.08 (C), 134.87 (CH), 136.26 (C), 137.18 (C), 138.55 (C), 139.33 (C), 144.85 (C), 193.15 (C) ppm; Long range ^{1}H-^{13}C correlations were observed between the carbonyl carbon (δ = 193.15) and 10-H (s, 8.13) and 1-H (dt, 7.71). The ^{1}H NMR assignment was based on NOESY experiment (300 MHz, $CDCl_3$) and HMBC experiments ($CDCl_3$, 75 MHz). EI-MS: *m*/*z* (%) = 244 (100) [M$^+$], 215 (43).

1-{3-Methoxy-5-methyl-2-[2-(trimethylsilyl)ethynyl]phenyl}-3-(2-methoxyphenyl)prop-2-yn-1-one (45): A mixture of **13** (218 mg, 0.58 mmol), and $BaMnO_4$ (444 mg, 1.73 mmol) in CH_2Cl_2 (15 mL) was stirred at 23 °C for 16 h. The mixture was filtered through celite, and washed with CH_2Cl_2. The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 5:1) to give **45** as a yellow solid (216 mg, 99%). M.p. 118–119 °C. R_f = 0.24 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.28 (s, 9 H), 2.47 (s, 3 H), 3.92 (s, 3 H), 3.95 (s, 3 H), 6.92 (s, 1 H), 6.94 (d, *J* = 8.1 Hz, 1 H), 6.98 (t, *J* = 7.5 Hz, 1 H), 7.45 (td, *J* = 8.2, 1.6 Hz, 1 H), 7.60 (dd, *J* = 7.7, 1.6 Hz, 1 H), 7.72 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = –0.12 (3 CH_3), 21.85 (CH_3), 55.73 (CH_3), 56.31 (CH_3), 89.84 (C), 92.34 (C), 92.34 (C), 98.63 (C), 105.03 (C), 108.71 (C), 109.56 (C), 110.77 (CH), 115.66 (CH), 120.52 (CH), 124.71 (CH), 132.39 (CH), 134.99 (CH), 139.32 (C), 140.56 (C), 161.42 (C), 161.70 (C), 177.50 (C) ppm.

4,9-Dimethoxy-2-methyl-11*H*-benzo[*b*]fluoren-11-one (46): A mixture of **45** (271 mg, 0.72 mmol), and phenol (678 mg, 7.20 mmol) in 1,2-dichlorobenzene (10 mL) was heated under reflux for 72 h. The mixture was cooled to room temperature and the solvent was evaporated. The residue was chromatographed (hexane/EtOAc, 5:1) to give **46** as a yellow solid (200 mg, 91%). M.p. 201–202 °C. R_f = 0.28 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.41 (s, 3 H), 3.99 (s, 3 H), 4.03 (s, 3 H), 6.79 (d, J = 7.3 Hz, 1 H), 6.88 (s, 1 H), 7.19 (s, 1 H), 7.38 (J = 7.3 Hz, 1 H), 7.43 (t, J = 7.3 Hz, 1 H), 8.02 (s, 1 H), 8.58 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.78 (CH_3), 55.55 (2 CH_3), 115.14 (CH), 117.02 (CH), 117.97 (CH), 120.12 (CH), 121.09 (CH), 121.93 (CH), 129.24 (CH), 138.10 (C), 138.19 (C), 138.41 (C), 141.04 (C), 155.96 (C), 157.80 (C), 193.64 (C) ppm (three signals were not observed due to overlapping). EI-MS: m/z (%) = 304 (100) [M^+], 289 (7), 261 (25). EI-HRMS: m/z for $C_{20}H_{16}O_3$: calcd. 304.1099; found 304.1102.

4-Methoxy-2-methyl-6*H*-benzo[*b*]fluorene-6,9,11-trione (47): H_5IO_6 (28 mg, 0.12 mmol) was dissolved in CH_3CN (1 mL) with vigorous stirring, and then CrO_3 (0.29 mg, 0.003 mmol) was added to the solution. The resulted solution was cooled to 0 °C. Compound **46** (9 mg, 0.03 mmol) was dissolved in CH_3CN (1 mL), and CH_2Cl_2 (2 mL) was added to the above solution. Immediately, the solution was orange, and a white precipitate formed. After 30 min stirring at 23 °C, the mixture was filtered, and the solvent was evaporated. The residue was chromatographed (hexane/EtOAc, 5:1) to give **47** as an orange solid (4 mg, 45%). M.p. 206–208 °C. R_f = 0.21 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.44 (s, 3 H), 4.06 (s, 3 H), 6.70 (s, 1 H), 7.02 (s, 2 H), 7.21 (s, 1 H), 8.30 (s, 1 H), 8.42 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 22.02 (CH_3), 55.81 (CH_3), 117.94 (CH), 118.96 (CH), 121.08 (CH), 121.90 (CH), 127.15 (C), 131.86 (C), 136.18 (C), 136.75 (C), 137.23 (C), 138.41 (CH), 138.94 (CH), 143.70 (C), 148.40 (C), 156.31 (C), 183.99 (CO), 184.98 (CO), 192.32 (CO) ppm. EI-MS: m/z (%) = 304 (100) [M^+], 261 (12), 222 (9). EI-HRMS: m/z for $C_{19}H_{12}O_4$: calcd. 304.0736; found 304.0746.

1-(2-Iodo-3-methoxy-5-methylphenyl)-3-(2-methoxyphenyl)prop-2-yn-1-ol (48): To a solution of 1-ethynyl-2-methoxybenzene (**14**) (200 mg, 1.51 mmol) in THF (10 mL) at 0 °C was added *n*BuLi (0.58 mL, 2.5 M solution in hexanes, 1.51 mmol). After 30 min, **17** (417 mg, 1.51 mmol) in THF (10 mL) was added, and the mixture was stirred at 23 °C for 5 h. The mixture was diluted with EtOAc, washed with a saturated NaCl solution, and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 5:1) to give **48** as a yellow solid (610 mg, 99%). M.p. 72–73 °C. R_f = 0.14 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.42 (s, 3 H), 2.89 (br. s, 1 H), 3.91 (s, 3 H), 3.92 (s, 3 H), 6.06 (s, 1 H), 6.67 (s, 1 H), 6.91 (d, J = 8.1 Hz, 1 H), 6.94 (td, J = 7.5, 1.1 Hz, 1 H), 7.34 (td, J = 7.5, 1.6 Hz, 1 H), 7.44 (s, 1 H), 7.48 (dd, J = 7.5, 1.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.42 (CH_3), 55.72 (CH_3), 56.57 (CH_3), 69.29 (CH), 83.16 (C), 86.87 (C), 92.33 (C), 110.69 (CH), 111.71 (C), 112.03 (CH), 120.36 (CH), 121.81 (CH), 129.98 (CH), 133.62 (CH), 139.79 (C), 143.92 (C), 157.98 (C), 160.24 (C) ppm. EI-MS: m/z (%) = 408 (77) [M^+], 281 (52) [M^+ – I]. EI-HRMS: m/z for $C_{18}H_{17}IO_3$: calcd. 408.0222; found 408.0228.

4-{2-[1-Hydroxy-3-(2-methoxyphenyl)prop-2-ynyl]-6-methoxy-4-methylphenyl}-2-methylbut-3-yn-2-ol (49): A mixture of **48** (731 mg, 1.79 mmol), 2-methyl-3-butyn-2-ol (158 mg, 1.88 mmol), [$Pd(PPh_3)_4$] (207 mg, 0.18 mmol), and CuI (26 mg, 0.18 mmol) in piperidine (10 mL) was stirred at 23 °C for 16 h. The mixture was diluted with Et_2O, and washed with saturated $NaHCO_3$ solution, HCl 10%, and H_2O, and dried (Na_2SO_4). The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 3:2) to give **49** as a yellow solid (554 mg, 85%): m.p. 143–144 °C; R_f = 0.1 (hexane/EtOAc, 3:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.68 (s, 6 H), 2.39 (s, 3 H), 3.48 (br. s, 1 H), 3.63 (d, J = 4.9 Hz, 1 H), 3.88 (s, 3 H), 3.90 (s, 3 H), 6.06 (d, J = 4.9 Hz, 1 H), 6.67 (s, 1 H), 6.89 (d, J = 8.3 Hz, 1 H), 6.91 (t, J = 7.5 Hz, 1 H), 7.29 (s, 1 H), 7.30 (td, J = 8.9, 1.8 Hz, 1 H), 7.43 (dd, J = 7.5, 1.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 22.02 (CH_3), 31.23 (CH_3), 31.34 (CH_3), 55.72 (CH_3), 55.94 (CH_3), 63.60 (CH), 65.62 (C), 75.90 (C), 82.37 (C), 92.66 (C), 103.58 (C), 107.55 (C), 110.66 (CH), 111.43 (C), 111.83 (C), 119.92 (CH), 120.42 (CH), 129.84 (CH), 133.67 (CH), 139.89 (C), 143.84 (C), 160.00 (C), 160.06 (C) ppm. ESI-TOF: m/z (%) = 387 [M^+ + Na]. ESI-TOF-HRMS: m/z for $C_{23}H_{24}NaO_4$: calcd. 387.1572; found 387.1566.

1-[2-(3-Hydroxy-3-methylbut-1-ynyl)-3-methoxy-5-methylphenyl]-3-(2-methoxyphenyl)prop-2-yn-1-one (50): A mixture of **49** (554 mg, 1.52 mmol) and $BaMnO_4$ (1.000 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was stirred at 23 °C for 16 h. The mixture was filtered through celite, and washed with CH_2Cl_2. The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 3:2) to give **50** as a yellow solid (467 mg, 85%): m.p. 91–92 °C; R_f = 0.26 (hexane/EtOAc, 3:2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.67 (s, 6 H), 3.50 (s, 3 H), 3.94 (s, 3 H), 3.99 (s, 3 H), 6.95 (s, 1 H), 6.98 (d, J = 7.5 Hz, 1 H), 7.02 (td, J = 7.5, 1.6 Hz, 1 H), 7.48 (td, J = 7.5, 1.6 Hz, 1 H), 7.63 (dd, J = 7.5, 1.6 Hz, 1 H), 7.79 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.89 (CH_3), 31.39 (2 CH_3), 55.89 (CH_3), 56.36 (CH_3), 65.95 (C), 89.84 (C), 92.45 (C), 103.64 (C), 109.66 (C), 109.67 (CH), 110.93 (CH), 115.84 (CH), 120.73 (CH), 125.12 (CH), 132.47 (CH), 135.05 (CH), 139.04 (C), 160.75 (C), 161.70 (C) ppm (three signals were not observed due to overlapping). EI-MS: m/z (%) = 362 (6) [M^+], 303 (20) [M^+ – C_3H_7O]. EI-HRMS: m/z for $C_{23}H_{22}O_4$: calcd. 362.1518; found 362.1522.

2,2,2-Trichloroethyl 4-{2-Methoxy-6-[3-(2-methoxyphenyl)propioloyl]-4-methylphenyl}-2-methylbut-3-yn-2-yl Carbonate (51): A mixture of **50** (50 mg, 0.14 mmol), 2,2,2-trichloroethyl chloroformate (31 mg, 0.15 mmol), DMAP (10 mg, 0.07 mmol) in pyridine (2 mL) was stirred at 23 °C for 16 h. The mixture was diluted with CH_2Cl_2, and washed with HCl (10%). The aqueous layer was extracted with Et_2O, dried (Na_2SO_4), and the solvents evaporated. The residue was chromatographed (hexane/EtOAc, 5:1) to give **51** as a yellow solid (26 mg, 36%). M.p. 101–102 °C. R_f = 0.18 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 6 H), 2.45 (s, 3 H), 3.87 (s, 3 H), 3.94 (s, 3 H), 4.78 (s, 2 H), 6.89 (s, 1 H), 6.92–6.99 (m, 2 H), 7.43 (td, J = 7.7, 1.8 Hz, 1 H), 7.58 (dd, J = 7.7, 2.0 Hz, 1 H), 7.76 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.89 (CH_3), 28.69 (2 CH_3), 55.83 (CH_3), 56.47 (CH_3), 76.39 (CH_2), 79.76 (C), 89.63 (C), 92.27 (C), 98.08 (C), 108.28 (C), 109.69 (C), 110.89 (CH), 116.10 (CH), 120.66 (CH), 122.06 (C), 124.91 (C), 125.26 (CH), 132.39 (CH), 135.05 (CH), 139.40 (C), 140.07 (C), 151.66 (C), 161.18 (C), 161.78 (C), 177.24 (C) ppm. EI-MS: m/z (%) = 422 (8) [M^+ – CCl_3], 344 (57) [M^+ – OTROC], 313 (100).

5-Methoxy-1-(2-methoxyphenyl)-3,7-dimethyl-9*H*-fluoren-9-one (52). Method A: A mixture of **50** (25 mg, 0.07 mmol), and $Sc(OTf)_3$ (34 mg, 0.07 mmol) in toluene (2 mL) was heated under reflux for 16 h. The mixture was cooled to room temperature, partitioned between H_2O, and CH_2Cl_2, washed with saturated NaCl solution, and dried (Na_2SO_4). The residue was cromatographed (hexane/EtOAc, 5:1) to give **52** as a yellow solid (6 mg, 25%). **Method B:** Compound **51** (12 mg, 0.02 mmol) in 1,2-dichlorobenzene (1.5 mL) was heated under reflux for 72 h. The mixture was cooled to room

temperature, and the solvent was evaporated. The residue was chromatographed (hexane/EtOAc, 5:1) to give **50** as a yellow solid (5 mg, 73%). M.p. 197–198 °C. R_f = 0.36 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.35 (s, 6 H), 2.42 (s, 3 H), 3.73 (s, 3 H), 3.98 (s, 3 H), 6.83 (s, 1 H), 6.89 (d, J = 0.7 Hz, 1 H), 6.96–7.04 (m, 3 H), 7.22 (dd, J = 7.5, 1.7 Hz, 1 H), 7.37 (dd, J = 7.5, 1.8 Hz, 1 H), 7.61 (d, J = 0.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.67 (CH_3), 22.05 (CH_3), 55.50 (2 CH_3), 110.57 (CH), 116.79 (CH), 117.68 (CH), 120.22 (CH), 123.84 (CH), 127.60 (C), 129.21 (CH), 130.11 (CH), 130.71 (CH), 136.69 (C), 137.22 (C), 140.62 (C), 144.65 (C), 144.86 (C), 155.07 (C), 157.03 (C), 220.00 (C) ppm (two signals were not observed due to overlapping). EI-MS m/z (%) 344 [M$^+$, 64], 313 (100). EI-HRMS: m/z for $C_{23}H_{20}O_3$: calcd. 344.1412; found 344.1425. The structure was confirmed by COSY, NOESY, HMQC, and HMBC experiments.

1-Ethynyl-2-methoxybenzene (14) and 4-Methoxy-6-methyl-3-methylidenephthalide (55): To a solution of **51** (64 mg, 0.18 mmol) in toluene (3 mL) was added NaOH (21 mg, 0.53 mmol), and the mixture was heated under reflux for 2 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2, washed with a saturated NaCl solution, and dried ($MgSO_4$). The solvent was evaporated to give a mixture of **14** and **55**. The products could be separated by flash column chromatography (hexane/EtOAc, 10:1). **14:** Yellow oil (9.6 mg, 42%): R_f = 0.5 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.31 (s, 1 H), 3.89 (s, 3 H), 6.88 (d, J = 8.4 Hz, 1 H), 6.91 (t, J = 7.5 Hz, 1 H), 7.32 (td, J = 8.2, 1.5 Hz, 1 H), 7.46 (dd, J = 9.1, 1.5 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 55.75 (CH_3), 80.05 (C), 81.07 (CH), 110.57 (CH), 111.13 (C), 120.39 (CH), 130.23 (CH), 134.11 (CH), 160.54 (C) ppm. **56:** White solid (8.4 mg, 25%). R_f = 0.21 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.48 (s, 3 H), 3.98 (s, 3 H), 5.24 (d, J = 2.0 Hz, 1 H), 5.41 (d, J = 1.8 Hz, 1 H), 6.97 (s, 1 H), 7.29 (s, 1 H) ppm. EI-MS: m/z (%) = 190 (100) [M$^+$], 119 (82). EI-HRMS m/z found for $C_{11}H_{10}O_3$: calcd. 190.0629, found 190.0626.

1-(2-Ethynyl-3-methoxy-5-methylphenyl)-3-(2-methoxyphenyl)prop-2-yn-1-ol (59): A mixture of **13** (152 mg, 0.40 mmol), and KF (84 mg, 1.45 mmol) in MeOH (5 mL) was stirred at 23 °C for 16 h. The mixture was diluted with CH_2Cl_2, washed with H_2O, and dried ($MgSO_4$). The solvent was evaporated, and the residue was cromatographed (hexane/EtOAc, 5:1) to give **59** as a yellow solid (125 mg, 99%). M.p. 78–80 °C. R_f = 0.1 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.40 (s, 3 H), 2.84 (d, J = 5.5 Hz, 1 H), 3.61 (s, 1 H), 3.88 (s, 3 H), 3.90 (s, 3 H), 6.10 (d, J = 4.7 Hz, 1 H), 6.70 (s, 1 H), 6.87 (d, J = 8.3 Hz, 1 H), 6.89 (td, J = 7.5, 1.0 Hz, 1 H), 7.27–7.31 (m, 1 H), 7.32 (s, 1 H), 7.44 (dd, J = 7.5, 1.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 22.11 (CH_3), 55.70 (CH_3), 56.01 (CH_3), 63.57 (CH), 77.60 (C), 82.89 (C), 86.20 (CH), 92.12 (C), 110.60 (CH), 111.39 (CH), 120.15 (CH), 120.32 (CH), 129.93 (CH), 133.73 (CH), 140.79 (C), 144.54 (C), 160.22 (C), 161.01 (C) ppm (two signals were not observed due to overlapping). EI-MS: m/z (%) = 306 (61) [M$^+$], 289 (23). EI-HRMS: m/z for $C_{20}H_{18}O_3$: 306.1256; found 306.1259.

1-(2-Ethynyl-3-methoxy-5-methylphenyl)-3-(2-methoxyphenyl)prop-2-yn-1-one (60): A mixture of **59** (125 mg, 0.41 mmol) and $BaMnO_4$ (524 mg, 2.04 mmol) in CH_2Cl_2 (15 mL) was stirred at 23 °C for 16 h. The mixture was filtered through celite, and washed with CH_2Cl_2. The solvent was evaporated, and the residue was chromatographed (hexane/EtOAc, 3:1) to give **60** as a yellow solid (118 mg, 97%). M.p. 144–145 °C. R_f = 0.21 (hexane/EtOAc, 3:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.47 (s, 3 H), 3.60 (s, 1 H), 3.93 (s, 3 H), 3.94 (s, 3 H), 7.26–6.92 (m, 3 H), 7.43 (td, J = 8.3, 1.7 Hz, 1 H), 7.59 (dd, J = 7.6, 1.6 Hz, 1 H), 7.76 (d, J = 0.6 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 21.91 (CH_3), 55.80 (CH_3), 56.34 (CH_3), 77.16 (C), 86.63 (CH), 90.21 (C), 92.33 (C), 109.55 (C), 110.79 (CH), 115.61 (CH), 120.61 (CH), 124.96 (CH), 132.45 (CH), 135.02 (CH), 139.75 (C), 140.70 (C), 161.78 (C), 177.34 (C) ppm (two signals were not observed due to overlapping). EI-MS: m/z (%) = 304 (23) [M$^+$], 289 (100). EI-HRMS: m/z for $C_{20}H_{16}O_3$: 304.1099; found 304.1095.

Acknowledgments

We thank the MEC (project CTQ2004-02869 and predoctoral fellowship to Ó. F.), the CAM (postdoctoral contract to C. M. and predoctoral fellowship to E. G.-C.) and the ICIQ foundation for support. We also acknowledge Dr. Diego J. Cárdenas for calculations on the rearrangement of Scheme 8 carried out with a simple model.

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Received: November 26, 2005
Published Online: January 12, 2006

