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SYNTHESIS OF INDENO[1,2-*b*]PHENANTHRENE-TYPE HETEROCYCLES BY CYCLOAROMATIZATION OF ACYCLIC NON-CONJUGATED BENZOTETRAYNES

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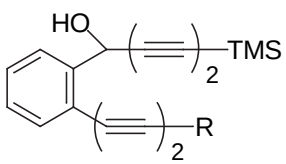
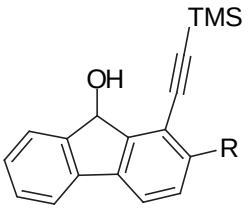
Abstract - A novel and simple procedure for the preparation of 6-oxa-, 6-thia-, and 6-azaindeno[1,2-*b*]phenanthrenes (**4**) by thermal cycloaromatization of acyclic non-conjugated benzotetraynes (**3**) is described.

The chemistry and biological activity of enediyne antitumor antibiotics continue to attract widespread attention in the scientific community.[1] In an extension of our research in this area, we synthesized new acyclic non-conjugated benzotetraynes (**1**) which undergo thermal cycloaromatization at room temperature to yield a fluorenol skeleton (**2**).[2] We now have successfully extended the reaction to the preparation of indeno[1,2-*b*]-phenanthrene-type heterocycles from acyclic non-conjugated benzotetraynes. We herein describe a novel and simple procedure for the preparation of 6-oxa-, 6-thia-, and 6-azaindeno[1,2-*b*]phenanthrenes (**4**) by thermal cycloaromatization of non-conjugated benzotetraynes (**3**) (Scheme 1).



1



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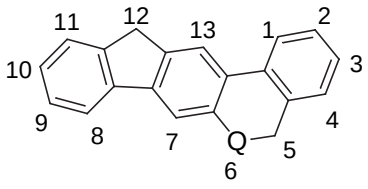


Q=O; 5,12-Dihydro-6-oxaindeno[1,2-*b*]phenanthrene
Q=S; 5,12-Dihydro-6-thiaindeno[1,2-*b*]phenanthrene
Q=NH; 5,12-Dihydro-6*H*-6-azaindeno[1,2-*b*]phenanthrene

Synthesis of 6-oxa-, 6-thia- and 6-azaindeno[1,2-*b*]phenanthrenes (4). Thermal cycloaromatization of 3.

Thermolysis of **3a** (50 mM) in dry benzene was carried out at 25 ˚C for 72 h in the dark under argon

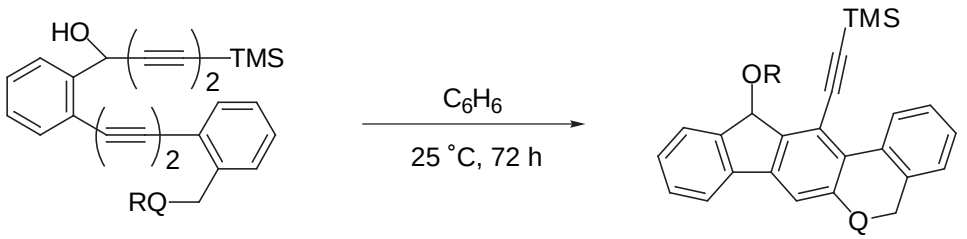
atmosphere (Table 1). Isolation and purification by silica gel column chromatography with benzene as an eluent gave 6-oxaindeno[1,2-*b*]phenanthrene derivative (**4a**) in 51% yield along with its *O*-methyl ether (**5**) in 40% yield. The reaction of **3b** under the same conditions yielded **4a** and its *O*-diphenylmethyl ether (**6**) in 47 and 14% yields, respectively, along with benzophenone in 5% yield. Thermolysis of **3c** under the same conditions yielded 6-thiaindeno[1,2-*b*]phenanthrene derivative (**4b**) in 19% yield and benzophenone in 10% yield, giving a large amount of unidentified oily products.

Scheme 1.

3: Q=O, S, NR^1

4: Q=O, S, NR^1

Table 1. Cycloaromatization of **3a**, **3b** and **3c**



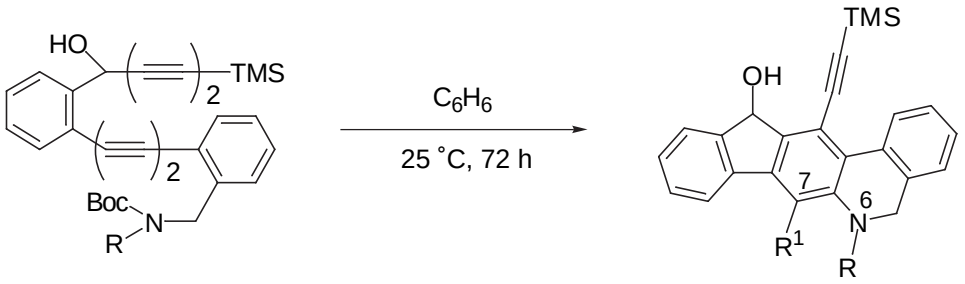
3a: R=CH_3, Q=O
3b: R=$CH(C_6H_5)_2$, Q=O
3c: R=$CH(C_6H_5)_2$, Q=S

4a: R=H, Q=O
4b: R=H, Q=S
5: R=CH_3, Q=O
6: R=$CH(C_6H_5)_2$, Q=O

Entry		Product (Yield %)
1	**3a**	**4a** (51), **5** (40)
2	**3b**	**4a** (47), **6** (12)
3	**3c**	**4b** (19)

Thermolysis of **3d** and **3e** was carried out under the same conditions as those used for **3a** (Table 2). The reaction of **3d** gave 6-azaindeno[1,2-*b*]phenanthrene derivative (**4c**) bearing two substituents of methyl at the 7-position and a Boc group at the 6-position in 57% yield and **4d** bearing a methyl group at the 6-position in 5% yields, respectively, without giving the corresponding *O*-alkyl ether derivatives. On the other hand, thermolysis of **3e** gave **4e** and **4f** in 24 and 13% yields, respectively, bearing two substituents of the diphenylmethyl and Boc groups at the 6- and 7-positions or *vice versa*.

Table 2. Cycloaromatization of **3d** and **3e**

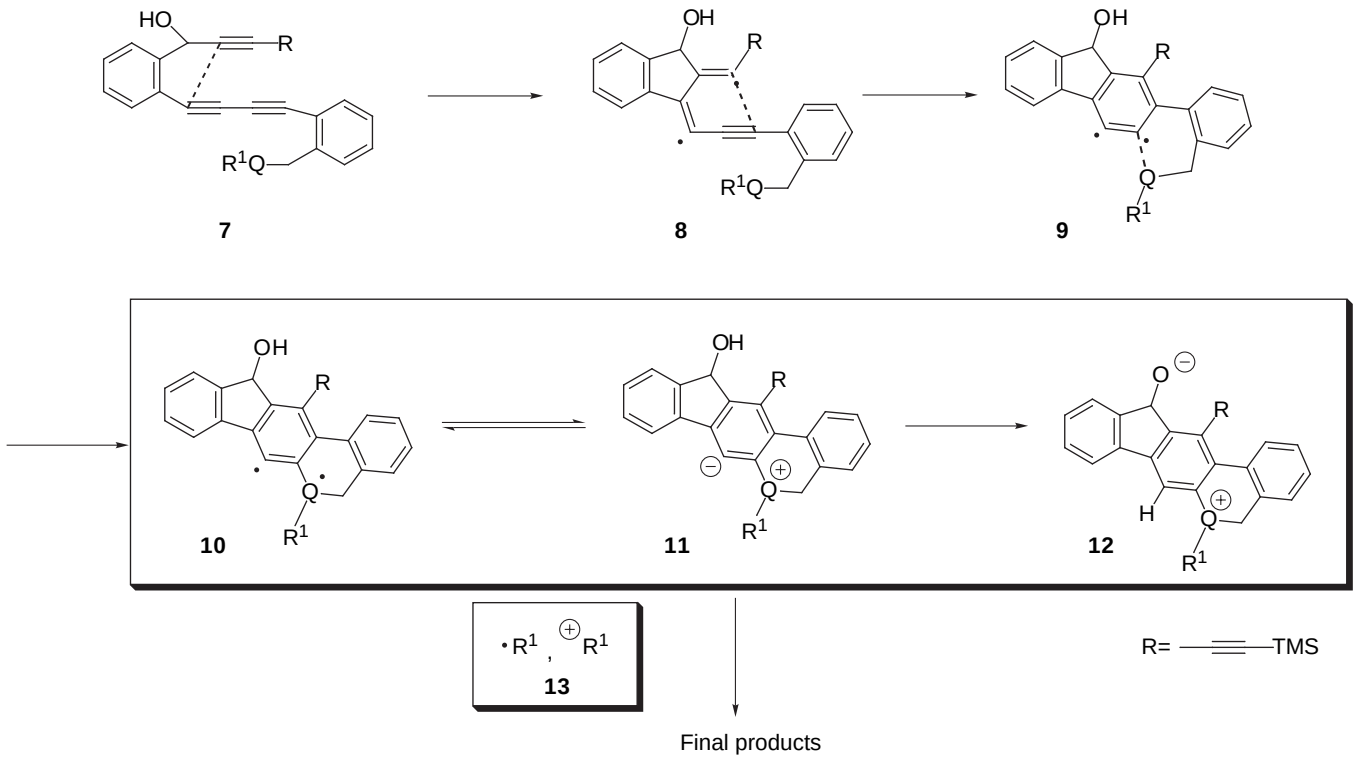


3d: R=CH_3
3e: R=$CH(C_6H_5)_2$

4c: R=Boc, R^1=CH_3
4d: R=CH_3, R^1=H
4e: R=Boc, R^1=$CH(C_6H_5)_2$
4f: R=$CH(C_6H_5)_2$, R^1=Boc

Entry		Product (Yield %)
1	**3d**	**4c** (57), **4d** (5)
2	**3e**	**4e** (24), **4f** (13)

Scheme 2.



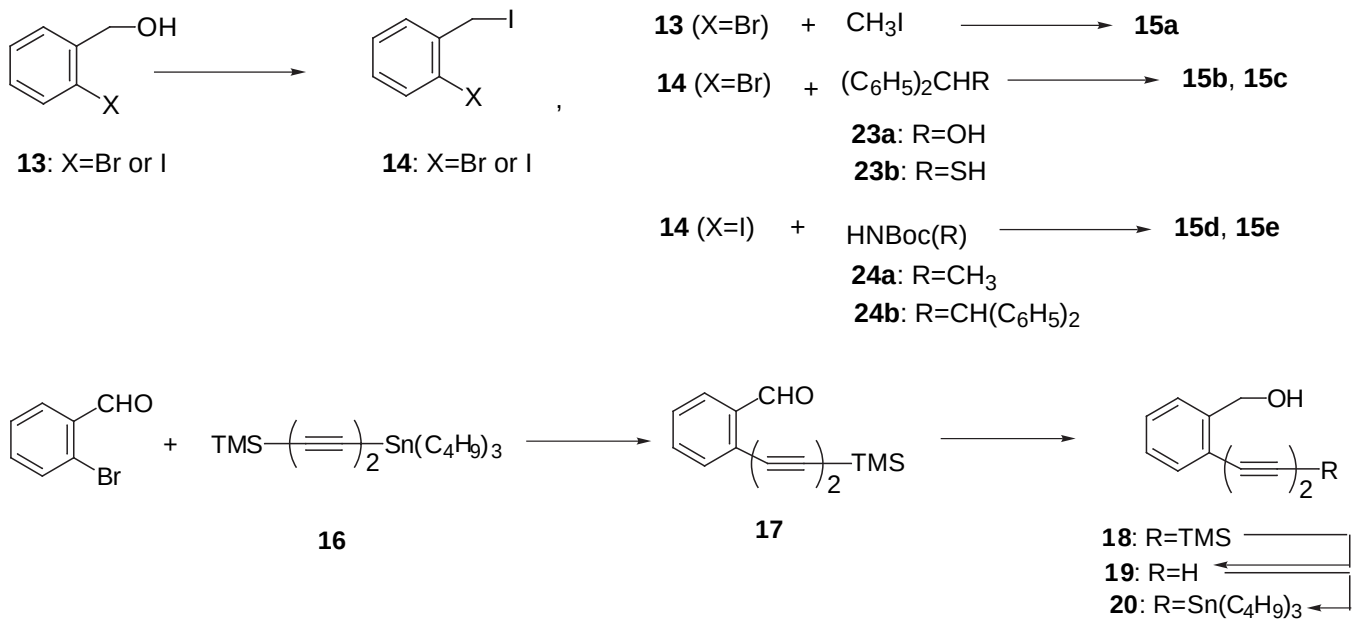
Although we do not have sufficient evidence to discuss the reaction mechanism of this cyclization,[2,3,4] a plausible mechanism of the overall transformation of **3** into the indeno[1,2-*b*]phenanthrene skeleton is

outlined in Scheme 2. At the first step, **7** gives an outer-ring diradical (**8**) generated by intramolecular annulation reaction between both buta-1,3-diyne functions of **7**. The diradical (**8**) undergoes further cyclization reaction to yield a fluorenol-1,2-benzyne intermediate (**9**). The formation of the *O*-alkyl ethers and benzophenone may indicate the generation of a diradical intermediate (**10**) and ionic intermediates (**11** and **12**) along with monoradical and carbocation intermediates (**13**). The active species (**10** and **11**) are generated simultaneously from **9**, and then the ionic intermediate (**11**) is converted into an ionic intermediate (**12**) through intermolecular hydrogen shift. These three active species are transformed into the final products.

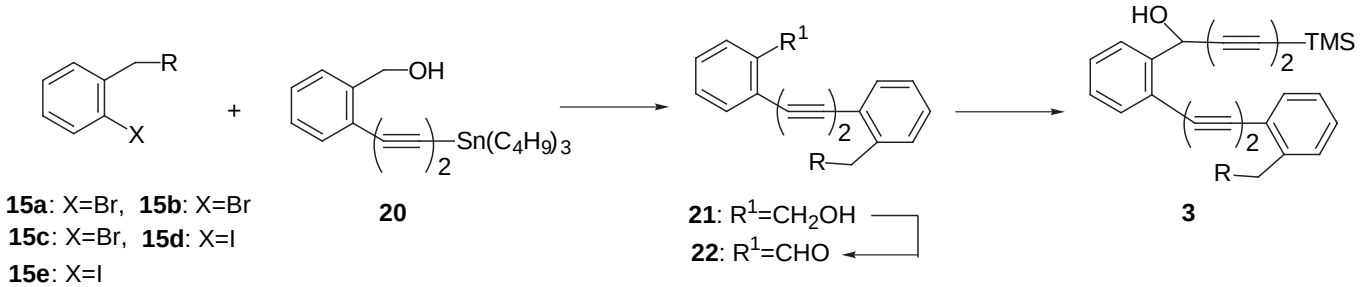
Synthesis of 3 and related intermediates.

Schemes 3 and 4 show an outline for the preparation of **3** and related intermediates.

Scheme 3.



Scheme 4.



a: R=OCH_3, **b**: R=$OCH(C_6H_5)_2$, **c**: R=$SCH(C_6H_5)_2$, **d**: R=$N(Boc)CH_3$, **e**: R=$N(Boc)CH(C_6H_5)_2$

Commercially available benzyl alcohols (**13**) were converted into benzyl iodides (**14**) according to the method described in the literature.[5] The key intermediates (**15**) were synthesized by the reaction of methyl

iodide and benzyl iodides (**14**) with sodium salts which were prepared from the corresponding alcohols (**13** and **23a**), thioalcohol (**23b**)[6] and *N-tert*-butoxycarbonyl derivatives (**24a**[7] and **24b**) and sodium hydride in dimethylformamide. The Stille coupling reaction[8] of a commercially available 2-bromobenzaldehyde with 1-trimethylsilyl-4-(tributylstannino)buta-1,3-diyne[9] (**16**) gave **17** in 91% yields. Sodium borohydride reduction of **17**, followed by removal of the protecting group of the trimethylsilyl group, yielded **19** in a quantitative yield. Compound (**20**), which was prepared *in situ* by reaction of **19** with tributyltin chloride, was allowed to react with **15** under the Stille conditions[8] to yield **21** in moderate to good yields. Oxidation of **21** with 2-iodoxybenzoic acid (IBX)[10] in dimethyl sulfoxide at room temperature yielded **22** in 76 to 90% yields. Reaction of **22** with 4-trimethylbuta-1,3-diyn-1-yllithium[11] in ether gave **3** in good yields. The reaction was completed in 5 min at room temperature. In order to avoid the following thermal cyclization reaction the reaction mixture was cooled to below 0 ˚C immediately after the reaction was completed, and all operations for the isolation and purification were performed at around 0 ˚C. The pure products were stored at a temperature below 0 ˚C.

In conclusion, a new method for the preparation of indeno[1,2-*b*]phenanthrene-type heterocycles has been developed by thermal cycloaromatization of non-conjugated benzotetraynes.

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded on samples dissolved in $CDCl_3$ on JEOL JNM-LA400 (400 MHz) spectrometer, operating at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. Chemical shifts are reported in δ (ppm) relative to TMS (δ = 0) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.0) for ^{13}C NMR. IR spectra were recorded on a Hitachi 260-30 infrared spectrophotometer. UV-VIS spectra were recorded on a Hitachi U-3210 spectrophotometer. MS spectra were measured on a JEOL JMS-600. All reactions were carried out under argon atmosphere, using dry and freshly distilled solvents under anhydrous conditions unless otherwise specified. Cycloaromatization of **3** was carried out in the dark. Flash column chromatography was performed using Merck 60 silica gel, 230-400 mesh. Commercially available 2-bromo- and 2-iodobenzaldehydes, 2-bromo- and 2-iodobenzyl alcohols (**13**) and benzhydrol (**23a**) were used without further purification.

Synthesis of 3. General procedure. 1-[2-[4-(2-Methoxymethylphenyl)buta-1,3-diyn-1-yl]phenyl]-6,6-dimethyl-6-silahepta-2,4-diyn-1-ol (3a). **Preparation of 4-trimethylbuta-1,3-diyn-1-yllithium**.[11] 1.5 M Methyllithium-lithium bromide complex in ether (4.9 mL, 4.7 mmol) was added to a solution of 1,4-bistrimethylsilylbuta-1,3-diyne[12] (2.8 g, 15 mmol) in dry ether (10 mL) at rt. The resulting mixture was stirred for 4 h to give 4-trimethylsilylbuta-1,3-diyn-1-yllithium. **Synthesis of 3a**. 4-trimethylbuta-1,3-diyn-1-yllithium, prepared by the method described above, was added dropwise to a solution of **22a** (1.0 g, 3.6 mmol) in dry ether (10 mL) using a 20 ml-syringe at rt. The resulting mixture was stirred for 5 min at rt and then chilled water was added. The mixture was extracted three times with ether. The extract was washed with chilled saturated aqueous NH_4Cl and brine, successively, and dried over $MgSO_4$. The following procedures were performed around 0 ˚C. After removal of the solvent, the residue was

purified by silica gel column chromatography with dichloromethane as an eluent to give pure **3a**. Yield: 1.2 g (83 %). Yellow oil. ^{1}H-NMR δ 7.69 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.44-7.36 (m, 2H), 7.34-7.25 (m, 2H), 5.94 (s, 1H), 4.67 (s, 3H), 2.81 (br s, 1H), 0.19 (s, 9H) ppm. ^{13}C-NMR δ 142.4, 141.5, 133.5, 133.2, 129.8, 129.5, 128.5, 127.5, 127.4, 126.9, 120.1, 120.0, 88.5, 87.2, 80.7, 79.2, 78.9, 77.7, 76.4, 72.4, 71.3, 62.9, 58.5, -0.6 ppm. IR (neat) ν: 2220, 2100 cm^{-1}. MS (FAB) m/z 445 (M^{+}).

1-[2-[4-(2-Diphenylmethoxymethylphenyl)buta-1,3-diyn-1-yl]phenyl]-6,6-dimethyl-6-silahepta-2,4-diyn-1-ol (3b). This compound was prepared from **22b** (0.40 g, 0.94 mmol) and the lithio derivative according to the method used for the preparation of **3a**. Yield: 0.50 g (97 %). Yellow oil. ^{1}H-NMR δ 7.70-7.68 (m, 1H), 7.62-7.51 (m, 3H), 7.44-7.25 (m, 14H), 5.87 (d, *J* = 5.4 Hz, 1H), 5.55 (s, 1H), 4.72 (s, 1H), 2.44 (d, *J* = 5.4 Hz, 1H), 0.19 (s, 1H) ppm. ^{13}C-NMR δ 142.4, 142.0, 141.8, 133.5, 129.8, 129.6, 128.7, 128.4, 128.2, 127.5, 127.2, 127.0, 120.3, 120.3, 88.7, 87.2, 83.3, 81.0, 79.1, 77.6, 76.3, 71.6, 69.0, 63.1, -0.5 ppm. IR (neat) ν: 3390, 2100 cm^{-1}. MS (FAB) m/z 547 [$(M-H)^{+}$].

1-[2-[4-(2-Diphenylmethylthiomethylphenyl)buta-1,3-diyn-1-yl]phenyl]-6,6-dimethyl-6-silahepta-2,4-diyn-1-ol (3c). This compound was prepared from **22c** (0.30 g, 0.68 mmol) and the lithio derivative according to the method used for the preparation of **3a**. Yield: 0.26 g (68 %). Yellow oil. ^{1}H-NMR δ 7.71-7.69 (m, 1H), 7.56-7.50 (m, 2H), 7.44-7.40 (m, 5H), 7.35-7.26 (m, 7H), 7.22-7.19 (m, 3H), 5.93 (d, *J* = 5.4 Hz, 1H), 5.12 (s, 1H), 3.79 (s, 2H), 2.58 (d, *J* = 5.4 Hz, 2H), 0.18 (s, 9H) ppm. ^{13}C-NMR δ 142.4, 141.6, 140.9, 133.6, 133.5, 129.8, 129.4, 128.7, 128.6, 128.4, 127.2, 127.0, 126.0, 121.4, 120.3, 88.7, 87.2, 81.2, 79.3, 79.2, 78.0, 76.3, 71.6, 63.1, 54.3, 35.3, -0.5 ppm. MS (FAB) m/z 565 [$(M+ H)^{+}$].

1-[2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-methylaminomethylphenyl)buta-1,3-diyn-1-yl]phenyl]-6,6-dimethyl-6-silahepta-2,4-diyn-1-ol (3d). This compound was prepared from **22d** (0.30 g, 0.80 mmol) and the lithio derivative according to the method used for the preparation of **3a**. Yield: 0.32 g (80 %). Brown oil. ^{1}H-NMR δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.45-7.24 (m, 5H), 5.96 (d, *J* = 5.4 Hz, 1H), 4.66 (br s, 1H), 2.92 (br s, 5/2H), 2.85 (br s, 3/2H), 1.50 (br s, 4H), 1.44 (br s, 5H), 0.19 (s, 9H) ppm. IR (neat) ν: 3400, 2120, 1678 cm^{-1}. MS (FAB) m/z 518 [$(M+Na)^{+}$].

1-[2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-diphenylmethylaminomethylphenyl])buta-1,3-diyn-1-yl]phenyl]-6,6-dimethyl-6-silahepta-2,4-diyn-1-ol (3e). This compound was prepared from **22e** (0.38 g, 0.72 mmol) and the lithio derivative according to the method used for the preparation of **3a**. Yield: 0.47 g (98 %). Brown oil. ^{1}H-NMR δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.35-6.77 (m, 15H), 6.60 (br s, 1H), 5.93 (d, *J* = 5.6 Hz, 1H), 4.74 (s, 2H), 2.53 (d, *J* = 5.6 Hz, 1H), 1.33 (s, 9H), 0.19 (s, 9H) ppm. ^{13}C-NMR δ 156.0, 142.6, 142.6, 142.3, 139.7, 133.3, 132.7, 129.7, 129.7, 128.9, 128.7, 128.4, 128.2, 127.2, 126.9, 126.1, 120.1, 119.1, 88.4, 87.3, 80.9, 80.5, 79.3, 78.9, 78.1, 76.6, 71.2, 63.9, 62.8, 47.2, 28.1, -0.6 ppm. IR (neat) ν: 3400, 2120, 1668 cm^{-1}.

MS (FAB) m/z 647 (M^+).

Synthesis of 6-oxaindeno[1,2-*b*]phenanthrenes (4a, 5 and 6) *via* cycloaromatization of 3a and 3b. **Cycloaromatization of 3a**. **12-Hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-oxa-indeno[1,2-*b*]phenanthrene (4a) and 12-methoxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-oxaindeno[1,2-*b*]phenanthrene (5).** Argon gas was bubbled through a solution of 3a (1.0 g, 2.5 mmol) and 1,4-cyclohexadiene (0.33 mL, 25 mmol) in benzene (50 mL) for 30 min. The resulting solution was stirred for 72 h at 25 ˚C under argon atmosphere. After removal of the solvent, the residue was purified by silica gel column chromatography with benzene as an eluent to give **4a** as the first elution and **5** as the second elution.

4a: Yield: 0.49 g (51 %). Yellow plates ($CHCl_3$-hexane): mp 63.6-63.8 ˚C. ^{1}H-NMR δ 8.78-8.76 (m, 1H), 7.70-7.68 (m, 1H), 7.63-7.61 (m, 1H), 7.43-7.31 (m, 1H), 7.30 (s, 1H), 7.23-7.21 (m, 1H), 5.84 (d, *J* = 3.3 Hz, 1H), 5.05 (d, *J* = 12.9 Hz, 1H), 5.04 (d, *J* = 12.9 Hz, 1H), 3.38 (d, *J* = 3.4 Hz, 1H), 0.36 (s, 9H) ppm. ^{13}C-NMR δ 156.8, 145.1, 143.6, 140.9, 138.9, 132.4, 129.7, 129.0, 128.4, 127.9, 127.7, 125.4, 125.2, 124.5, 123.3, 120.3, 115.5, 110.1, 104.4, 102.8, 74.5, 9.0, -0.4 ppm. IR (KBr) : 3564, 2139 cm^{-1}. MS (FAB) m/z 382 (M^+). UV-VIS (CH_3CN): λmax (log ε) 365 (4.12), 317 (4.25), 304 (4.20), 277 (4.10), 254 (4.37), 226 (4.21) nm. *Anal.* Calcd for $C_{25}H_{22}O_2Si$: C, 78.50; H, 5.80. Found: C, 78.47; H, 5.52. **5**: Yield: 0.40 g (40 %). Brown oil. ^{1}H-NMR δ 8.91-8.89 (m, 1H), 7.41-7.19 (m, 6H), 5.63 (s, 1H), 5.06 (d, *J* = 12.7 Hz, 1H), 4.99 (d, *J* = 12.7 Hz, 2H), 3.27 (s, 3H), 0.33 (s, 9H) ppm. ^{13}C-NMR δ 157.0, 144.1, 141.7, 140.4, 139.7, 132.5, 129.9, 129.0, 128.2, 127.8, 127.6, 125.9, 125.2, 124.4, 123.7, 120.1, 117.5, 109.5, 103.9, 102.2, 81.6, 69.1, 54.0, -0.3 ppm. IR (neat) ν: 2209, 1700 cm^{-1}. MS (FAB) m/z 396 (M^+). *Anal*. Calcd for $C_{26}H_{24}O_2Si$: C, 78.75; H, 6.10. Found: C, 78.70; H, 6.35.

Cycloaromatization of 3b. **4a and 12-diphenylmethoxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-oxaindeno[1,2-*b*]phenanthrene (6)**. A solution of **3b** (0.54 g, 1.0 mmol) and 1,4-cyclohexadiene (0.13 mL, 10 mmol) in benzene (20 mL) was allowed to react under the same conditions as those used for **3a**. The reaction mixture was worked up according to the method used for **3a** to give **4a**, **6** and benzophenone.

4a: Yield: 0.34 g (47 %). Yellow plates ($CHCl_3$-hexane): mp 63.6-63.8 ˚C. **6**: Yield: 40 mg (12%). Colorless needles (benzene-hexane): mp 144.1-144.3 ˚C. ^{1}H-NMR δ 8.66-8.64 (m, 1H), 7.53-7.51 (m, 1H), 7.36-7.12 (m, 15H), 7.10-7.06 (m, 1H), 6.88-6.87 (m, 1H), 5.95 (s, 1H), 5.64 (s, 1H), 5.03 (d, *J* = 12.7 Hz, 1H), 4.96 (d, *J* = 12.7 Hz, 1H), 0.23 (s, 9H) ppm. ^{13}C-NMR δ 156.9, 143.5, 143.2, 143.1, 141.6, 141.5, 139.8, 132.5, 129.9, 128.9, 128.5, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.1, 126.7, 126.3, 126.2, 124.3, 124.1, 119.8, 117.6, 109.3, 103.5, 103.5, 81.1, 80.0, 69.1, -0.4 ppm. IR (KBr) ν: 2147 cm^{-1}. MS (FAB) m/z 549 [$(M+H)^+$]. *Anal*. Calcd for $C_{38}H_{32}O_2Si$: C, 83.17; H, 5.88. Found: C, 82.91; H, 5.59. **Benzophenone**: Yield: 24 mg (5%). Colorless powders: mp 48-49 ˚C.

Cycloaromatization of 3c. **12-Hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-thiaindeno-[1,2-*b*]phenanthrene (4b)**. A solution of **3c** (0.26 g, 0.46 mmol) and 1,4-cyclohexadiene (0.13 mL, 10

mmol) in benzene (20 mL) was allowed to react under the same conditions as those used for **3a**. The reaction mixture was worked up according to the method used for **3a** to give **4b** and benzophenone.

4b: Yield: 34 mg (19 %). Yellow powders (CH_2Cl_2-hexane): mp 74.6-76.2 °C. ^{1}H-NMR δ 8.25-8.22 (m, 1H), 7.51 (s, 1H), 7.49-7.47 (m, 1H), 7.42-7.40 (m, 1H), 7.22-7.06 (m, 5H), 5.63 (d, *J* = 2.7 Hz, 1H), 3.60 (d, *J* = 13.7 Hz, 1H), 3.52 (d, *J* = 13.7 Hz, 1H), 3.27 (d, *J* = 2.7 Hz, 1H), 0.09 (s, 9H) ppm. ^{13}C-NMR δ 148.1, 144.8, 139.1, 138.6, 137.9, 135.4, 135.0, 133.1, 129.2, 129.2, 128.5, 128.3, 126.6, 126.1, 125.4, 120.6, 120.3, 117.1, 103.9, 102.9, 74.7, 32.6, -0.4 ppm. IR (KBr)ν: 3560, 2155 cm^{-1}. MS (FAB) m/z 647 $(M)^+$. UV-VIS (CH_3CN): λmax (log ε) 367 (3.83), 305 (4.31), 275 (4.50), 225 (4.35) nm. *Anal.* Calcd for $C_{25}H_{22}OSSi$: C, 75.33; H, 5.56; S, 8.04. Found: C, 75.36; H, 5.51; S, 7.85.

Benzophenone: Yield: 8 mg (9.5 %). Colorless powders: mp 48.0-49.0 °C.

Cycloaromatization of 3d. Synthesis of 6-*tert*-butoxycarbonyl-7-methyl-12-hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-azaindeno[1,2-*b*]phenanthrene (4c) and 6-methyl-12-hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-azaindeno[1,2-*b*]phenanthrene (4d). Reaction of **3d** (0.30 g, 0.61 mmol), 1,4-cyclohexadiene (0.08 mL, 6.1 mmol) in benzene (12.2 mL) under the same conditions as those used for **3a** gave **4c** and **4d**.

4c: Yield: 172 mg (57 %). Yellow plates (CH_2Cl_2-hexane): mp 224.9-225.2 °C (decomp). ^{1}H-NMR δ 8.74-8.71 (m, 1H), 7.70-7.65 (m, 2H), 7.40-7.34 (m, 4H), 7.26-7.24 (m, 1H), 5.80 (d, *J* = 2.9 Hz, 1H), 4.06 (d, *J* = 15.4 Hz, 1H), 4.01 (d, *J* = 15.4 Hz, 1H), 3.50 (d, *J* = 2.9 Hz, 1H), 2.53 (s, 3H), 1.70 (s, 9H), 0.34 (s, 9H) ppm. ^{13}C-NMR δ 167.8, 147.4, 146.7, 144.9, 137.8, 135.7, 134.1, 130.5, 130.2, 129.0, 128.4, 128.2, 127.7, 126.8, 126.6, 126.5, 125.2, 121.9, 116.2, 104.7, 102.8, 82.6, 74.2, 55.2, 41.5, 28.2, -0.4 ppm. IR (KBr) ν: 2140, 1723 cm^{-1}. MS (FAB) m/z 496 $[(M+H)^+]$. UV-VIS (CH_3CN): λmax (log ε) 358 (4.02), 321 (4.43), 308 (4.40), 273 (4.49), 248 (4.34), 226 (4.40) nm. *Anal.* Calcd for $C_{31}H_{33}NO_3Si$: C, 75.12; H, 6.71; N, 2.83. Found: C, 75.02; H, 6.59; N, 2.99. **4d**: Yield: 12 mg (5%). Yellow oil. ^{1}H-NMR δ 8.76 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 1H), 7.42-7.27 (m, 4H), 7.26 (s, 1H), 7.20 (d, *J* = 6.8 Hz, 1H), 5.82 (d, *J* = 2.4 Hz, 1H), 4.08 (s, 2H), 3.42 (d, *J* = 2.4 Hz, 1H), 3.04 (s, 3H), 0.34 (s, 9H) ppm. ^{13}C-NMR δ 149.7, 145.3, 140.4, 139.7, 134.7, 131.3, 128.9, 128.0, 127.4, 126.7, 126.4, 125.2, 125.1, 124.4, 119.8, 115.5, 104.9, 103.8, 103.3, 74.6, 55.5, 39.5, -0.3 ppm. IR (neat) ν: 3510 cm^{-1}. MS (FAB) m/z 394 (M^+). *Anal.* Calcd for $C_{26}H_{25}NOSi$: C, 78.94; H, 6.37; N, 3.54. Found: C, 79.20; H, 6.65; N, 3.33.

Cycloaromatization of 3e. Synthesis of 6-*tert*-butoxycarbonyl-7-diphenylmethyl-12-hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-azaindeno[1,2-*b*]phenanthrene (4e) and 6-diphenylmethyl-7-*tert*-butoxycarbonyl-12-hydroxy-13-(3,3-dimethyl-3-silabutyn-1-yl)-6-azaindeno[1,2-*b*]phenanthrene (4f). Reaction of **3e** (0.47 g, 0.73 mmol), 1,4-cyclohexadiene (0.095 mL, 7.3 mmol) in benzene (14.6 mL) under the same conditions as those used for **3a** gave **4e** and **4f**.

4e: Yield: 113 mg (24 %). Yellow powders (CH_2Cl_2-hexane): mp 157.2-158.0 °C. ^{1}H-NMR δ 8.30-8.26 (m, 1H), 7.79-7.76 (m, 1H), 7.73-7.70 (m, 1H), 7.38-7.35 (m, 2H), 7.21-7.13 (m, 5H), 7.00-6.96 (m, 7H), 6.71-6.68 (m, 1H), 5.89 (s, 1H), 5.80 (d, *J* = 2.7 Hz, 1H), 4.43 (d, *J* = 15.9 Hz, 1H), 4.39 (d, *J* = 15.9 Hz,

1H), 3.60 (d, J = 2.7 Hz, 1H), 1.43 (s, 9H), 0.29 (s, 9H) ppm. ^{13}C-NMR δ 167.4, 145.9, 145.3, 144.9, 140.0, 139.8, 138.2, 136.5, 135.9, 131.8, 131.0, 129.1, 129.0, 128.7, 128.3, 127.6, 127.5, 127.4, 126.9, 126.8, 126.3, 125.6, 125.5, 125.2, 122.5, 116.1, 104.2, 103.2, 83.3, 74.1, 71.6, 48.7, 28.3, -0.4 ppm. IR (KBr) ν: 2145, 1718 cm^{-1}. MS (FAB) m/z 647 (M^+). UV-VIS (CH_3CN): λmax (log ε) 321 (4.33), 303 (4.40), 291 (4.43), 277 (4.46) nm. *Anal.* Calcd for $C_{43}H_{41}NO_3Si \cdot H_2O$: C, 77.56; H, 6,51; N, 2.10. Found: C, 77.29; H, 6.40; N, 2.10. **4f**: Yield: 62 mg (13 %). Pale yellow powders (CH_2Cl_2-hexane): mp 198.9-199.4 °C. ^{1}H-NMR (50 °C) δ 8.78 (d, J = 8.1 Hz, 1H), 7.63-7.61 (m, 1H), 7.45-7.36 (m, 5H), 7.31-7.11 (m, 10H), 6.92 (d, J = 7.3 Hz, 1H), 6.88 (s, 1H), 5.82 (d, J = 2.7 Hz, 1H), 4.07 (s, 2H), 3.43 (d, J = 2.7 Hz, 1H), 1.45 (s, 9H), 0.35 (s, 9H) ppm. ^{13}C-NMR (50°C) δ 172.0, 147.8, 144.9, 141.6, 141.3, 140.5, 139.5, 138.4, 136.8, 132.0, 128.8, 128.4, 128.3, 128.0, 127.9, 127.8, 127.4, 127.1, 127.0, 126.7, 126.5, 126.3, 125.0, 124.1, 119.7, 115.6, 111.3, 103.8, 103.1, 83.1, 76.2, 74.6, 51.7, 28.0, -0.3 ppm. IR (KBr) ν: 2130, 1720 cm^{-1}. MS (FAB) m/z 647 (M^+). UV-VIS (CH_3CN): λmax (log ε) 361 (4.34), 344 (4.20), 320 (4.69), 306 (4.48), 281 (4.57), 225 (4.60) nm. *Anal.* Calcd for $C_{43}H_{41}NO_3Si$: C, 79,72; H, 6,38; N, 2.16. Found: C, 79.36; H, 6.13; N, 2.36.

Compounds (**14**) were synthesized according to the method described in the literature.

2-Iodobenzyl iodide[5] **(14: X=I)**. Yield: 77%. Colorless crystals (hexane): mp 70.5-73.0 °C. ^{1}H-NMR δ 7.81 (dd, J = 8.1, 1.2 Hz, 1H), 7.48 (dd, J = 7.6, 1.5 Hz, 1H), 7.29 (td, J = 7.6, 1.2 Hz, 2H), 6.93 (td, J = 7.6, 1.5 Hz, 1H), 4.55 (s, 2H) ppm.

2-Bromobenzyl iodide[5] **(14: X=Br)**. Yield: 80 %. Colorless needles (hexane): mp 40.6-40.9 °C. ^{1}H-NMR δ 7.53 (dd, J = 8.1, 1.2 Hz, 1H), 7.44 (dd, J = 7.6, 1.5 Hz, 1H), 7.26 (td, J = 6.6, 1.2 Hz, 2H), 7.13 (td, J = 8.1, 1.7 Hz, 1H), 4.55 (s, 2H) ppm.

2-Bromobenzyl methyl ether (15a).[13] NaH (705 mg; 60% dispersion as mineral oil, 17.6 mmol) was added to a solution of **13** (X=Br) (3.0 g, 16.0 mmol) in dry THF (60 mL) at 0 °C over 10 min. The mixture was stirred for 30 min and then a solution of methyl iodide (1.1 g, 17.6 mmol) in dry THF (5 mL) was added. The resulting mixture was stirred for 30 min at rt, poured onto ice-water and extracted three times with benzene. The benzene layer was washed with saturated aqueous NH_4Cl and brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography with benzene as an eluent to give pure **15a**. Yield: 2.4 g (75%). Colorless oil. ^{1}H-NMR δ 7.52 (td, J = 7.8, 1.1 Hz, 2H), 7.45 (dd, J = 7.6, 1.5 Hz, 1H), 7.30 (td, J = 7.3, 0.98 Hz, 1H), 7.13 (td, J = 8.1, 1.7 Hz, 1H), 4.51 (s, 2H), 3.45 (s, 1H). ^{13}C-NMR δ 137.5, 132.4, 128.9, 128.8, 127.3, 122.6, 73.8, 58.5 ppm.

2-Bromobenzyl diphenylmethyl ether (15b). This compound was prepared from benzhydrol (**23a**) (3.1 g, 16.8 mmol) and **14** (X=Br) (5.3 g, 17.9 mmol) according to the method used for the preparation of **15a**. Yield: 5.6 g (99%). Colorless oil. ^{1}H-NMR δ 7.73-7.71 (m, 1H), 7.64-7.62 (m, 1H), 7.54-7.46 (m, 4H), 7.45-7.42 (m, 4H), 7.40-7.35 (m, 2H), 7.26-7.22 (m, 1H), 5.63 (s, 1H), 4.72 (s, 2H) ppm. ^{13}C-NMR δ 141.9, 137.8, 132.4, 129.1, 128.8, 128.4, 127.5, 127.3, 127.1, 122.6, 83.3, 70.2 ppm. MS

(FAB) m/z 375 [(M+Na)$^+$]. *Anal*. Calcd for $C_{20}H_{17}OBr$: C, 68.00; H, 4.85; Br, 22.62. Found: C, 67.74; H, 4.85; Br, 22.38.

2-Bromobenzyl diphenylmethyl sulfide (15c). A mixture of **23b** (1.5 g, 7.5 mmol), **14** (X=Br) and KF (1.0 g, 7.5 mmol) in DMF (10 mL) was vigorously stirred for 2 h at 25 ˚C and poured into water. The resulting mixture was extracted three times with ether. The extract was washed with saturated aqueous NH_4Cl and brine, and dried over $MgSO_4$. After removal of the solvent, an oily material was purified by silica gel column chromatography with benzene as an eluent to give **15c**. Yield: 2.4 g (95%). Colorless oil. ^{1}H-NMR (50 ˚C) δ 7.55-7.52 (m, 1H), 7.42-7.40 (m, 4H), 7.33-7.28 (m, 4H), 7.25-7.15 (m, 4H), 7.10-7.06 (m, 1H), 5.09 (s, 1H), 3.69 (s, 1H) ppm. ^{13}C-NMR (50 ˚C) δ 140.9, 137.4, 133.1, 130.7, 128.6, 128.5, 128.3, 127.2, 124.7 ppm. MS (FAB) m/z 391 [(M+Na)$^+$]. *Anal*. Calcd for $C_{20}H_{17}BrS$: C, 65.04; H, 4.64; S, 8.68; Br, 21.64. Found: C, 65.29; H, 4.53; S, 8.47; Br, 21.91.

(*N*-*tert*-Butoxycarbonyl-*N*-methyl)-2-iodobenzylamine (15d). NaH (30 mg; 60% dispersion as mineral oil, 0.75 mmol) was added to a solution of **24a** (100 mg, 0.75 mmol) in dry DMF (5 mL) at 0˚C. The mixture was vigorously stirred for 30 min at 0 ˚C and **14** (X=I; 308 mg, 0.90 mmol) was added dropwise over 1 h. The resulting mixture was allowed to stand for 2.5 h at ambient temperature with vigorous stirring, poured into water and extracted three times with ether. The extract was washed with saturated aqueous NH_4Cl and brine, successively and dried $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography with a (5:1) mixture of benzene and ethyl acetate as an eluent to give pure **15d**. Yield: 198 mg (76%). Colorless oil. ^{1}H-NMR δ 7.81 (dd, *J* = 7.8 Hz, 1.0, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 4.44 (s, 2H), 2.86 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C-NMR δ 155.2, 139.4, 139.0, 128.3, 128.0, 127.8, 127.0, 79.1, 56.9, 34.0, 28.0 ppm. IR (KBr) ν: 1682 cm^{-1}. MS (FAB) m/z 466 (M$^+$). *Anal.* Calcd for $C_{13}H_{18}NO_2I$: C, 44.97; H, 5.23; N, 4.03; I, 36.55. Found: C, 45.13; H, 5.02; N, 4.05; I, 36.61.

(*N*-*tert*-Butoxycarbonyl-*N*-diphenylmethyl)-2-iodobenzylamine (15e). This compound was prepared from **24b** (1.0 g, 3.5 mmol) and **14** (X=I; 1.4 g, 4.2 mmol) according to the method for the preparation of **15d**. Yield: 1.6 g (92%). Colorless oil. ^{1}H-NMR δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.25-7.17 (m, 10H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.1 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.57 (br s, 1H), 4.48 (s, 2H), 1.34 (s, 9H) ppm. ^{13}C-NMR δ 156.0, 140.2, 139.8, 138.6, 128.7, 128.2, 127.8, 127.6, 127.4, 127.2, 97.1, 80.4, 64.0, 54.2, 28.2 ppm. IR (KBr) ν: 1690 cm^{-1}. MS (EI) m/z 499 (M$^+$). HRMS Calcd for $C_{25}H_{26}NO_2I$: 499.1009. Found: 499.0985.

1-Trimethylsilyl-4-(tributylstannino)buta-1,3-diyne (16)[9]**.** A solution of 1.5 M methyllithium-lithium bromide complex in ether (110 mL, 0.16 mol) was added to a solution of 1,4-bistrimethylsilylbuta-1,3-diyne[12] (47 g, 0.24 mol) in dry ether (500 mL) at rt. The resulting mixture was stirred for 5 h and tributyltin chloride (78.1 g, 0.24 mol) was added dropwise over 30 min at 0 ˚C. The mixture was stirred for 2 h at rt. After removal of volatile materials under a reduced pressure of 10 mmHg, the residue was dissolved into benzene (1 L) and filtered on Celite®. The filtrate was evaporated under the reduced pressure to give **16** which was used for the following process without further purification.

2-(5,5-Dimethyl-5-silahexa-1,3-diyn-1-yl)benzaldehyde (17). A mixture of 2-

bromobenzaldehyde (12 mL, 96 mmol), **16**, prepared from 1,4-bistrimethylsilylbuta-1,3-diyne by the method described above, and $PdCl_2(PPh_3)_2$ (3.0 g, 5.0 mmol) in toluene (300 mL) was gradually heated to110 ˚C and vigorously stirred for 2 h at 110 ˚C and then cooled to rt. 2N Aqueous KF was added to the reaction mixture, which was stirred for 30 min and filtered on Celite®. The filtrate was dried over $MgSO_4$ and evaporated to give an oily material which was purified by silica gel column chromatography with a (10:1) mixture of benzene and hexane as an eluent to give pure **17**. Yield: 20 g (91%). Brown solid (benzene): mp 32.4-33.6 ˚C. ^{1}H-NMR δ 10.47 (s, 1H), 7.93-7.91 (m, 1H), 7.63-7.61 (m, 1H), 7.58-7.54 (m, 1H), 7.51-7.46 (m, 1H), 0.26 (s, 9H) ppm. ^{13}C-NMR δ 190.8, 137.6, 134.5, 133.7, 129.5, 127.5, 124.8, 93.5, 87.1, 80.7, 72.0, -0.5 ppm. MS (FAB) m/z 227 [$(M+H)^+$]. IR(KBr) ν: 2202, 2100, 1695 cm^{-1}. *Anal.* Calcd for $C_{14}H_{14}OSi$: C, 74.29; H, 6.23. Found: C, 74.15; H, 6.10.

2-(Buta-1,3-diyn-1-yl)benzyl alcohol(19) *via* 18. A small portion of $NaBH_4$ (1.1 g, 30 mmol) was added to a solution of **17** (14 g, 60 mmol) in methanol (80 mL) at 0 ˚C. The mixture was stirred for 10 min at 0 ˚C and then K_2CO_3 (0.83 g, 6.0 mmol) was added. The mixture was vigorously stirred for 30 min at 0˚C and neutralized with 1N HCl. After removal of the solvent, the residue was extracted three times with benzene. The benzene layer was washed with saturated aqueous $NaHCO_3$ and brine, successively, and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel column chromatography with benzene as an eluent to give pure **19**. Yield: 9.0 g (100 %). Colorless needles (benzene): mp106-109 ˚C. ^{1}H-NMR δ 7.33-7.27 (m, 2H), 7.22-7.17 (m, 1H), 7.08-7.04 (m, 1H), 4.63 (d, *J* = 5.4 Hz, 2H), 2.38 (s, 1H), 2.06 (t, *J* = 5.4 Hz, 1H) ppm. ^{13}C-NMR δ 144.4, 133.5, 129.9, 127.4, 127.2, 118.9, 77.8, 72.8, 72.5, 67.8, 63.3 ppm. MS (FAB) m/z 156 (M^+). IR(KBr) ν: 3280, 2204 cm^{-1}. *Anal.* Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.37; H, 4.88.

2-(4-Tributylstanninobuta-1,3-diyn-1-yl)benzyl alcohol (20). A mixture of di-*iso*-propylamine (8.1 g, 80 mmol) and tributyltin chloride (13.0 g, 40 mmol) was vigorously stirred for 30 min at rt and then **19** (1.8 g, 11.6 mmol) was added. The resulting mixture was vigorously stirred for 24 h at rt and filtered to remove inorganic materials. The filtrate was evaporated to give **20** (6.0 g) which was used for the following process without further purification.

Synthesis of 21. **General procedure**. **2-[4-(2-Methoxymethylphenyl)buta-1,3-diyn-1-yl]benzyl alcohol (21a).** A mixture of **15a** (1.1 g, 5.8 mmol), **20** (6.0 g) and $PdCl_2(PPh_3)_2$ (0.14 g, 0.19 mmol) in toluene (50 mL) was gradually heated to 110 ˚C and vigorously stirred for 2 h at 110 ˚C and then cooled to rt. Two normal (2N) aqueous KF (10 ml) was added to the reaction mixture, which was stirred for 30 min and filtered on Celite®. The filtrate was dried over $MgSO_4$ and evaporated to give an oily material which was purified by silica gel column chromatography with benzene as an eluent to give pure **21a**. Yield: 0.36 g (34%). Pale blue powders (benzene-hexane): mp 79.1-79.8 ˚C. ^{1}H-NMR δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 4.83 (d, *J* = 4.6 Hz, 2H), 4.64 (s, 2H), 3.45 (s, 3H), 2.57 (t, *J* = 4.6 Hz, 1H) ppm. ^{13}C-NMR δ 144.0, 141.4, 133.1, 133.1, 129.5, 129.4, 127.5, 127.4, 127.3, 127.1, 120.1, 119.6, 80.3, 79.9, 78.1, 77.8, 72.4, 63.3, 58.5 ppm. IR (KBr) ν: 3250, 2210 cm^{-1}. MS (FAB) m/z 276 (M^+). *Anal.* Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83. Found: C, 82.51; H, 5.85.

2-[4-(2-Diphenylmethoxymethylphenyl)buta-1,3-diyn-1-yl]benzyl alcohol (21b). This compound was prepared from **15b** (0.56 g, 3.8 mmol), **20** (4.0 g) and $PdCl_2(PPh_3)_2$ (0.095 g, 0.13 mmol) in toluene (34 mL) according to the method used for the preparation of **21a**. Yield: 1.1 g (70 %). Colorless

powders (benzene-hexane): mp 107.1-107.6 ˚C. ^{1}H-NMR δ 7.64-7.57 (m, 1H), 7.53-7.50 (m, 2H), 7.47-7.41 (m, 5H), 7.38-7.31 (m, 7H), 7.26-7.22 (m, 3H), 5.53 (s, 1H), 4.80 (d, *J* = 5.9 Hz, 2H), 4.72 (s, 2H), 2.16 (d, *J* = 5.9 Hz, 1H) ppm. ^{13}C-NMR δ 144.0, 141.9, 141.7, 133.2, 133.1, 129.5, 129.4, 128.4, 128.3, 128.1, 127.5, 127.4, 127.4, 127.1, 120.4, 119.7, 83.3, 80.6, 79.8, 78.3, 77.7, 68.9, 63.4 ppm. IR (KBr) ν: 3465, 2141 cm^{-1}. MS (FAB) m/z 451 (M^+). *Anal.* Calcd for $C_{31}H_{24}O_2$: C, 86.89; H, 5.65. Found: C, 87.02; H, 5.55.

2-[4-(2-Diphenylmethylthiomethylphenyl)buta-1,3-diyn-1-yl]benzyl alcohol (21c). This compound was prepared from **15c** (0.70 g, 4.5 mmol), **20** (4.7 g) and $PdCl_2(PPh_3)_2$ (0.11 g, 0.15 mmol) in toluene (39 mL) according to the method used for the preparation of **21a**. Yield: 1.3 g (64 %). Brown oil. ^{1}H-NMR (50 ˚C) δ 7.57-7.55 (m, 1H), 7.52-7.49 (m, 2H), 7.443-7.38 (m, 5H), 7.32-7.18 (m, 10H), 5.12 (s, 1H), 4.87 (d, *J* = 4.4 Hz, 2H), 3.78 (s, 2H), 2.00 (br s, 1H) ppm. ^{13}C-NMR (50 ˚C) δ 144.0, 141.6, 140.9, 133.6, 133.2, 129.6, 129.4, 129.3, 128.6, 128.5, 127.5, 127.3, 127.2, 127.0, 121.5, 119.9, 80.8, 80.0, 78.4, 78.1, 63.6, 54.3, 35.4 ppm. MS (FAB) m/z 444 (M^+). IR(neat) ν: 3375, 2200, 2130 cm^{-1}. *Anal.* Calcd for $C_{31}H_{24}OS$: C, 83.75; H, 5.44; S, 7.21. Found: C, 83.83; H, 5.52; S, 7.49.

2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-methylaminomethylphenyl)buta-1,3-diyn-1-yl]benzyl alcohol (21d). This compound was prepared from **15d** (0.45g, 2.9 mmol), **20** (2.4 g) and $PdCl_2(PPh_3)_2$ (0.07 g, 0.096 mmol) in toluene (25 mL) according to the method used for the preparation of **21a**. Yield: 0.61 g (57 %). Yellow oil. ^{1}H-NMR δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 6.0 Hz, 1H), 7.27-7.21 (m, 3H), 4.88 (d, *J* = 6.0 Hz, 2H), 4.66 (s, 2H), 2.88 (br s, 3H), 2.16 (t, *J* = 6.0 Hz, 1H), 1.47 (s, 9H) ppm. ^{13}C-NMR δ 154.8, 144.5, 141.3, 136.4, 132.6, 132.1, 128.5, 127.4, 126.1, 126.0, 126.0, 120.2, 118.8, 80.1, 80.0, 78.4, 78.0, 77.8, 62.1, 50.0, 33.2, 27.4 ppm. IR (KBr) ν: 3424, 2214, 2141, 1681 cm^{-1}. HRMS. Calcd for $C_{24}H_{25}NO_3$ 375.1835. Found: 375.1850.

2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-diphenylmethylaminomethylphenyl)buta-1,3-diyn-1-yl]benzyl alcohol (21e). This compound was prepared from **15e** (0.47g, 3.0 mmol), **20** (3.1 g) and $PdCl_2(PPh_3)_2$ (0.072 g, 0.10 mmol) in toluene (26 mL) according to the method used for the preparation of **21a**. Yield: 0.83 g (79 %). Brown oil. ^{1}H-NMR δ 7.50 (t, *J* = 9.0 Hz, 2H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.27-7.16 (m, 11H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.01 (br s, 1H), 6.50 (br s, 1H), 4.84 (d, *J* = 6.1 Hz, 2H), 4.74 (s, 2H), 2.07 (t, *J* = 6.1 Hz, 1H), 1.32 (s, 9H) ppm. ^{13}C-NMR δ 156.1, 144.2, 142.5, 140.0, 133.2, 132.8, 129.5, 128.9, 128.8, 128.2, 127.4, 127.3, 127.2, 126.9, 126.2, 120.0, 119.4, 80.8, 80.5, 80.0, 78.3, 78.3, 64.1, 63.6, 47.5, 28.2 ppm. IR (KBr) ν: 3450, 1695 cm^{-1}. MS (FAB) m/z 528 [$(M+H)^+$]. *Anal.* Calcd for $C_{36}H_{33}NO_3$: C, 81.95; H, 6.30; N, 2.65. Found: C, 81.55; H, 6.46; N, 2.80.

Synthesis of 22. General procedure. 2-[4-(2-Methoxymethlyphenyl)buta-1,3-diyn-1-yl]benzaldehyde (22a). IBX[11] (0.46 g, 1.6 mmol) was added to a solution of **21a** (0.45 g, 1.6 mmol) in DMSO (9 mL) at rt. The resulting mixture was vigorously stirred for 30 min and then water was added. The mixture was extracted three times with ethyl acetate. The extract was washed with brine, dried over $MgSO_4$ and evaporated to give an oily material which was purified by silica gel column chromatography with a (20:1) mixture of benzene and ethyl acetate to give pure **22a**. Yield: 0.40 g (90 %). Colorless needles (benzene): mp 53.6-54.0 ˚C. ^{1}H-NMR δ 10.52 (s, 1H), 7.94-7.92 (m, 1H), 7.66-7.25 (m, 7H), 4.66 (s, 2H), 3.48 (s, 3H) ppm. ^{13}C-NMR δ 190.7, 141.8, 137.3, 134.2, 133.6, 133.2, 129.7, 129.4, 128.2, 127.5, 127.4,

125.0, 119.7, 81.4, 80.3, 77.8, 72.4, 58.5 ppm. IR (KBr) ν: 2209, 1700 cm^{-1}. MS (FAB) m/z 297 $(M)^+$. *Anal*. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.33; H, 5.04.

2-[4-(2-Diphenylmethoxymethylphenyl)buta-1,3-diyn-1-yl]benzaldehyde (22b). This compound was prepared from **21b** (1.0 g, 2.3 mmol) and IBX (662 mg, 2.3 mmol) according to the method used for the preparation of **22a**. Yield: 0.94 g (94 %). Yellow powder (benzene): mp 107.4-108.0 ˚C. ^{1}H-NMR δ 10.48 (s, 1H), 7.95-7.93 (m, 1H), 7.63-7.54 (m, 4H), 7.49-7.45 (m, 1H), 7.43-7.38 (m, 5H), 7.35-7.31 (m, 4H), 7.29-7.22 (m, 3H), 5.53 (s, 1H), 4.73 (s, 2H) ppm. ^{13}C-NMR δ 190.8, 141.9, 137.3, 134.2, 133.7, 133.3, 129.8, 129.4, 128.4, 128.2, 127.5, 127.1, 125.2, 120.0, 83.3, 81.6, 80.5, 77.7, 77.3, 68.9 ppm. IR (KBr) ν: 2212, 1695 cm^{-1}. MS (FAB) m/z 427 (M^+). *Anal.* Calcd for $C_{31}H_{22}O_2$: C, 87.30; H, 5.20. Found: C, 87.16; H, 5.19.

2-[4-(2-Diphenylmethylthiomethylphenyl)buta-1,3-diyn-1-yl]benzaldehyde (22c). This compound was prepared from **21c** (0.1 g, 0.23 mmol) and IBX (0.63 g, 0.23 mmol) according to the method used for the preparation of **22a**. Yield: 86 mg (86 %). Yellow prisms (benzene-hexane): mp 88.7-89.3 ˚C. ^{1}H-NMR δ 10.52 (s, 1H), 7.97-7.95 (m, 1H), 7.68-7.66 (m, 1H), 7.61-7.57 (m, 1H), 7.54-7.48 (m, 2H), 7.43-7.41 (m, 4H), 7.34-7.19 (m, 9H), 5.10 (s, 1H), 3.79 (s, 2H) ppm. ^{13}C-NMR δ 190.9, 141.8, 140.9, 137.3, 134.2, 133.8, 133.7, 129.6, 129.4, 129.4, 128.6, 128.4, 128.3, 127.5, 127.2, 127.1, 125.3, 121.2, 81.8, 80.6, 77.9, 77.7, 54.2, 35.3 ppm. IR (KBr) ν: 2225, 1690 cm^{-1}. MS (FAB) m/z 465 $[(M+ Na)^+]$. *Anal.* Calcd for $C_{31}H_{22}OS$: C, 84.13; H, 5.01; S, 7.24. Found: C, 83.97; H, 4.81; S, 7.02.

2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-methylaminomethylphenyl)buta-1,3-diyn-1-yl]benzaldehyde (22d). This compound was prepared from **21d** (0.5 g, 1.3 mmol) and IBX (0.37 g, 1.3 mmol) according to the method used for the preparation of **22a**. Yield: 0.38 g (76 %). Brown oil. ^{1}H-NMR δ 10.52 (d, *J* = 0.5 Hz, 1H), 7.95-7.93 (m, 1H), 7.66-7.64 (m, 1H), 7.59-7.54 (d, *J* = 6.0 Hz, 1H), 7.27-7.21 (m, 3H), 4.88 (d, *J* = 6.0 Hz, 2H), 4.66 (s, 2H), 2.88 (br s, 3H), 2.16 (t, *J* = 6.0 Hz, 1H), 1.47 (s, 9H) ppm. ^{13}C-NMR δ 188.1, 154.6, 141.6, 137.2, 136.4, 133.2, 132.7, 132.0, 128.9, 128.2, 126.8, 126.1, 123.8, 119.7, 81.2, 79.8, 78.2, 77.8, 77.4, 49.9, 31.2, 27.4 ppm. MS (FAB) m/z 396 $[(M+Na)^+]$. *Anal*. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 76.48; H, 6.11; N, 3.73.

2-[4-(2-*N*-*tert*-Butoxycarbonyl-*N*-diphenylmethylaminomethylphenyl)buta-1,3-diyn-1-yl]benzaldehyde (22e). This compound was prepared from **21d** (0.83 g, 1.6 mmol) and IBX (0.44 g, 1.6 mmol) according to the method used for the preparation of **22a**. Yield: 0.76 g (92 %). Colorless powders: mp 145.2-145.5 ˚C. ^{1}H-NMR (50 ˚C) δ 10.49 (s, 1H), 7.93 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.56 (td, *J* = 7.6, 1.5 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.35-7.33 (s, 1H), 7.27-7.14 (m, 11H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.02 (br s, 1H), 4.75 (s, 2H), 1.33 (s, 9H) ppm. ^{13}C-NMR (50 ˚C) δ 190.7, 156.1, 142.8, 139.9, 137.5, 134.2, 133.6, 132.9, 129.4, 129.2, 128.8, 128.3, 127.6, 127.2, 127.0, 126.2, 125.3, 119.0, 81.8, 80.5, 80.5, 78.0, 77.9, 64.1, 47.5, 28.2 ppm. IR (KBr) ν: 2225, 1690 cm^{-1}. MS (FAB) m/z 525 (M^+). *Anal.* Calcd for $C_{36}H_{31}NO_3$: C, 82.26; H, 5.94; N, 2.66. Found: C, 82.48; H, 5.68; N, 2.78.

Diphenylmethanethiol (23b) was prepared from **23a** (10.0 g, 54 mmol) and Lawesson's reagent (22.0 g, 54 mmol) according to the method described in the literature.[6] Blue oil: bp 111 ˚C (0.15 mmHg) [lit., bp 140 ˚C (1.5 mmHg)]. ^{1}H-NMR δ 7.41 (d, *J* = 7.6 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 4H), 7.23 (t, *J* = 7.2 Hz, 2H), 5.45 (d, *J* = 5.1 Hz, 1H), 2.27 (d, *J* = 5.1 Hz, 1H) ppm.

(*N*-*tert*-Butoxycarbonyl)methylamine (24a) was synthesized according to the method described in the literature.[7] Yield: 90 %. Colorless oil. ^{1}H-NMR δ 4.47 (br s, 1H), 2.73 (d, *J* = 4.9 Hz, 3H), 1.45 (s, 9 H) ppm.

(*N*-*tert*-Butoxycarbonyl)diphenylmethylamine (24b) was synthesized according to the method used for the preparation of **24a**. Yield: 82%. Colorless needles (benzene-hexane): mp 113.8-114.4 ˚C. ^{1}H-NMR δ 7.34-7.30 (m, 4H), 7.27-7.24 (m, 1H), 5.92 (br s, 1H), 5.17 (br s, 1H), 1.44 (br s, 1H) ppm. MS (FAB) m/z 306 [$(M+Na)^+$]. IR (KBr) ν: 3375, 1694 cm^{-1}. *Anal*. Calcd for $C_{18}H_{21}NO_2$: C, 76.30; H, 7.47; N, 4.94. Found: C, 76.18; H, 7.52; N, 4.94.

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