3α-(Hydroxymethyl)-2β,6α-dimethyl-1β-(methoxycarbonyl)cyclohexane-2α-carboxylic Acid γ-Lactone (49). A mixture of **47** (40 mg, 0.18 mmol) and 5 mg of Adams' catalyst in 3 mL of methanol was stirred under a hydrogen atmosphere until gas uptake had ceased. Filtration and evaporation of the solvent afforded 40 mg (98%) of **49**: IR (film) 2950, 1775, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30 (1 H, d, J = 2 Hz), 4.20 (1 H, d, J = 4 Hz), 3.75 (3 H, s), 2.6–2.2 (2 H, m), 2.35 (1 H, d, J = 11 Hz), 2.1–1.6 (4 H, m), 1.33 (3 H, s), 0.98 (3 H, d, J = 6 Hz); mass spectrum, m/e 226.121 (M^+, calcd for $C_{12}H_{18}O_4$ 226.121).

***trans,trans*-2,4-Hexadienyl Tetrolate (51).** A solution of tetrolic acid (1.64 g, 20 mmol) and 4 mL of oxalyl chloride in 20 mL of dry benzene was heated to 50 °C for 1 h. Careful concentration in vacuo (20 °C bath) afforded a brown oil. This oil was added slowly to a solution of sorbyl alcohol (**19**; 1.96 g, 20 mmol) and pyridine (2 mL, 25 mmol) in 20 mL of benzene at 0 °C. After being stirred at room temperature for 4 h, the mixture was diluted with ether, and the ethereal layer was washed with saturated $CuSO_4$ solution, water, and saturated NaCl solution. The ethereal extracts were dried over $MgSO_4$, filtered, and evaporated to give an oil. Column chromatography (30% ethyl acetate–hexane) of this material afforded 1.0 g (50%) of sorbyl alcohol and 1.20 g (42%) of **51**: IR (film) 2950, 2250, 1710, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.4–5.4 (4 H, m), 4.65 (2 H, d, J = 6 Hz), 1.96 (3 H, s), 1.76 (3 H, d, J = 6 Hz); mass spectrum, m/e 164 (M^+).

3α-(Hydroxymethyl)-1,6α-dimethylcyclohexa-1,4-diene-carboxylic Acid γ-Lactone (52). A solution of 1.20 g (7.3 mmol) of **51** and 100 mg of 2,6-di-*tert*-butyl-*p*-cresol was refluxed for 24 h under a nitrogen atmosphere. After cooling, the solvent was removed in vacuo to yield 1.25 g (96%) of a light brown oil which was shown by TLC to be virtually pure **52**. Column chromatography (30% ethyl acetate–hexane) provided an analytically pure sample of **52**: IR (Nujol) 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.72 (2 H, s), 4.55 (1 H, dd, J = 7, 7 Hz), 3.75 (1 H, dd, J = 7, 10 Hz), 3.7–3.3 (1 H, m), 3.15–2.75 (1 H, m), 2.21 (3 H, t, J = 1.5 Hz), 1.25 (3 H, d, J = 7 Hz); mass spectrum, m/e 162.069 ($M^+ - H_2$, calcd for $C_{10}H_{10}O_2$ 162.068).

3α-(Hydroxymethyl)-1,6α-dimethylcyclohex-1-ene-carboxylic Acid γ-Lactone (54). A suspension of 50 mg of platinum oxide in 25 mL of ethyl acetate was stirred under a hydrogen atmosphere until hydrogen uptake had stopped, and a solution of **52** (710 mg, 4.3 mmol) in 5 mL of ethyl acetate was added by syringe. Stirring was initiated, and the mixture took up 4.3 mmol of hydrogen over a period of 35 min. At this point, gas uptake slowed, and the reaction mixture was removed from the hydrogen atmosphere and filtered. Evaporation of the solvent in vacuo afforded 685 mg (95%) of **54**: IR (film) 2950, 2870, 1775, 1679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.46 (1 H, dd, J = 8, 8 Hz), 3.77 (1 H, dd, J = 8, 10 Hz), 3.1–2.7 (1 H, m), 2.5–2.2 (1 H, m), 2.13 (3 H, d, J = 2 Hz), 2.0–1.6 (4 H, m), 1.12 (3 H, d, J = 7 Hz); mass spectrum, m/e 166.100 (M^+, calcd for $C_{10}H_{14}O_2$ 166.099).

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Registry No. 19, 17102-64-6; **20**, 616-02-4; **21**, 71028-72-3; **22**, 71028-71-2; **23**, 71028-73-4; **24**, 71028-74-5; **25**, 71140-69-7; **26**, 71028-76-7; **29**, 71028-78-9; **30**, 71028-80-3; **31**, 77044-48-5; **32**, 77044-49-6; **33**, 71028-81-4; **34**, 77044-50-9; **35**, 77044-51-0; **36**, 77044-52-1; **37**, 77044-53-2; **38**, 77044-54-3; **39**, 77044-55-4; **40**, 77044-56-5; **41**, 77044-57-6; **42**, 77044-58-7; **43**, 77044-59-8; **44**, 77044-60-1; **45**, 77044-61-2; **46**, 77044-62-3; **47**, 77044-63-4; **48**, 77044-64-5; **49**, 77060-43-6; **50**, 590-93-2; **51**, 77044-65-6; **52**, 77044-66-7; **54**, 77044-67-8; 1,10-dimethyl-3,5-dioxatricyclo[5.3.1.$0^{4,1}$]undecane, 77044-68-9; *trans*-2,4-pentadienol, 51042-92-3; 1β-formyl-3α-(hydroxymethyl)-1α,6α-dimethylcyclohexane-2α-carboxylic acid γ-lactone, 77044-69-0.

Facile Synthesis of Ethynylated Benzoic Acid Derivatives and Aromatic Compounds via Ethynyltrimethylsilane†

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The coupling reaction between an aromatic halide and ethynyltrimethylsilane under the catalysis of palladium(0) generated in situ, followed by treatment of the (trimethylsilyl)ethynyl product with potassium carbonate in methanol at ambient temperatures, provides a simple approach to various ethynylated benzoic acid derivatives and other aromatic compounds. The conditions for the removal of the trimethylsilyl group were very mild, so that base-sensitive functionalities on the aromatic moiety could be tolerated.

Classical methods[1] for the synthesis of terminal arylacetylenes in general involve manipulation of preformed, two-carbon side chains and include methods such as the Vilsmeier method,[2-4] the halogenation–dehydrohalogenation sequence of vinyl aromatics[5] and ketones,[6,7] and the dehydrohalogenation of β,β-dihalo olefins.[8,9] Other methods that deviate from the classical approach have utilized the decomposition of preconstructed heterocyles.[10,11] A recent innovation in the synthesis of arylacetylenic compounds has been the use of protecting groups.[12] Acetylene, protected at one end, can be introduced onto an aromatic nucleus via coupling at the free end. Subsequent removal of the protecting group generates a terminal arylacetylene.

The widely accepted procedure for the introduction of an acetylenic substituent onto an aromatic nucleus is the Stephens–Castro coupling reaction[13-15] between an aryl

† During the preparation of this manuscript, a report on a similar method appeared.[52]

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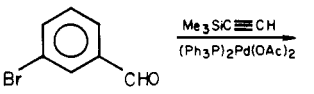
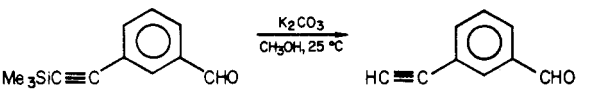
iodide and a protected cuprous acetylide in pyridine at reflux. Commonly used[16] protecting groups are acetals,[17,18] ketones,[19] ketals,[20] hydroxymethyl,[21,22] tetrahydropyran-protected hydroxymethyl,[22,23] dimethylcarbinol, ethyl vinyl ether protected carbinol,[24,25] and ethyl ester.[26] The removal of these groups often requires several steps and/or strongly alkaline media.

An elegant alternative to the Stephens–Castro methods rests in the coupling[27] between arylcopper reagents and (iodoethynyl)trimethylsilane[28] at below ambient temperatures. The removal of the trimethylsilyl group with alkali is quantitative.[29] However, the in situ preparation of the arylcopper reagents depends on prior formation of Grignard or lithium reagents, a requirement that forbids the presence of functional groups which are incompatible with these organometallic reagents.

Our studies in acetylene-terminated aromatic and heteroaromatic oligomers[30] necessitated the development of an efficient procedure for the synthesis of ethynylated compounds. This report describes the palladium-catalyzed coupling reaction between aryl halides and ethynyltrimethylsilane[31] to give trimethylsilylethynylated intermediates which yield ethynylated aromatic compounds after removal of the trimethylsilyl group with potassium carbonate at ambient temperatures. Triethylamine[32] is not only used as the solvent but also as a scavenger for the hydrogen halide generated during the ethynylation reaction. The isolation of the insoluble amine salt provides a quantitative measure of the extent of the reaction. In the event that the substrate was not completely soluble, toluene was used as the cosolvent.

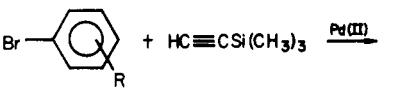
The benzoic acid derivatives in general gave high overall yields of the eventual ethynylated products. For example, when 3-bromobenzaldehyde was mixed with an excess of ethynyltrimethylsilane in deaerated triethylamine and warmed to 80–90 °C in the presence of a catalytic amount of a mixture of palladium acetate and triphenylphosphine, a quantitative yield of triethylamine hydrobromide was obtained. After workup and distillation, 3-[(trimethylsilyl)ethynyl]benzaldehyde was obtained in 80% yield. Subsequent treatment of 3-[(trimethylsilyl)ethynyl]benzaldehyde with anhydrous potassium carbonate in anhydrous methanol at 25 °C gave a quantitative yield of 3-ethynylbenzaldehyde (entry 1, Table I).



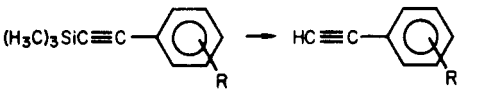


This synthetic method appears to be quite general. The methodology is simple and the use of the expensive palladium compound is justified by its function as a catalyst.

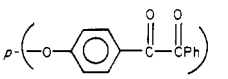
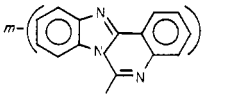
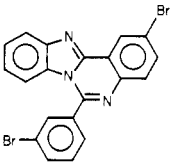
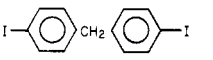
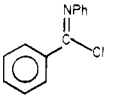
Table I. Palladium-Catalyzed Ethynylation



1-10



TMSE TE

entry	R	% yield[b] TMSE	% yield[b] terminal acetylene (TE)
1	*m*-CHO	80	84
2	*p*-CHO	99	100
3	*o*-CHO	75	80
4	*m*-CO_2CH_3	70	71
5	*p*-CO_2CH_3	69	73
6	*m*-CF_3	67	60
7	2-F, 5-NO_2	78	50[d,e]
8	2-F, 5-NH_2	*c*	*f*
9[a]		88	56
10		71	95
11		76	100
12		81	100
13		78	90

[a] Obtained from Dr. P. M. Hergenrother, NASA-Langley. [b] All reported yields are isolated yields. [c] The ethynylation step did not go to completion. [d] The deprotection reaction did not yield the expected product. [e] The isolated product from the reaction of 7-TMSE was 1-ethynyl-2-methoxy-5-nitrobenzene. [f] A 50% overall yield of pure 8-TE from 7 was obtained by iron reduction of 7-TMSE to 8-TMSE and subsequent deprotection.

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The synthesis of 1-phenyl-2-propyn-1-one anil (entry 13, Table I) suggests a facile entry to ethynyl ketones from acid chlorides. Indeed, the coupling of aroyl chlorides with phenylacetylene has been demonstrated in the presence of a palladium catalyst.[33,34]

Our procedure is derived from the Heck reaction[35] between phenylacetylene and aromatic halides in the presence of organopalladium catalysts and is complementary to existing methods of synthesis of terminal arylacetylenes. Noteworthy is that base-sensitive functional groups such as aldehydes and esters present on the aromatic halides are not affected during the transformation. A parallel procedure in effecting ethynylation of aromatic compounds employs the palladium-catalyzed coupling of aromatic bromides and iodides with 2-methyl-3-butyn-2-ol.[36,37] Since the removal of the acetonyl protecting group requires sodium hydroxide in refluxing toluene, base-sensitive groups cannot be present.

In accordance with the original Heck reaction,[35] electron-withdrawing groups present on the aromatic halide facilitate the palladium-catalyzed coupling reaction, while electron-donating groups impart adverse effects. A likely mechanism for the reaction involves the prior reduction of palladium(II) acetate by two acetylide ions to yield the Glaser diacetylene product[38] and a palladium(0) species which initiates the catalytic cycle. Oxidative addition[39] of the aromatic bromide to palladium(0) is a facile process, generating arylpalladium(II) bromide, which is then attacked by another acetylide ion to yield an unstable aryl(σ-ethynyl)palladium(II) intermediate. Reductive elimination of the arylated acetylene regenerates the palladium(0) species to maintain the catalytic cycle. The detailed mechanism of the oxidative addition step between the aryl halide and palladium(0) has been suggested as being nucleophilic aromatic substitution,[40] electron-transfer,[41] or three-center[42] in nature. It is noteworthy that the nucleophilic nature of the low-valent metals is emphasized in all three mechanisms proposed.

Experimental Section

Nuclear magnetic resonance (NMR) spectra were taken on a Varian EM-360L spectrometer with tetramethylsilane as an internal standard. Infrared (IR) spectra were taken on a Beckman IR-5 spectrometer. Mass spectra were performed by West Coast Technical Service, Inc. Elemental analyses were performed by Galbraith Laboratories, Inc.

Starting Materials. Ethynyltrimethylsilane was prepared according to a literature procedure[31] or purchased from Silar Laboratories, Inc. 1-Bromo-2-fluoro-5-nitrobenzene[43-45] was prepared by nitration (100% yield) of commercial 1-bromo-2-fluorobenzene. Iron reduction of 1-bromo-2-fluoro-5-nitrobenzene gave 3-bromo-4-fluoroaniline (64–78% yield). 4-(4-Bromophenoxy)benzil was a generous gift from Dr. P. M. Hergenrother (NASA, Langley). 6-(3-Bromophenyl)benzimidazoquinazoline (**10**) was synthesized from 2-(2-aminophenyl)benzimidazole and 3-bromobenzaldehyde by adaptation of a literature procedure[46] (79% yield). By the same procedure, 10-bromo-6-(3-bromophenyl)benzimidazoquinazoline (**11**) was prepared from 2-(2-amino-5-bromophenyl)benzimidazole and 3-bromobenzaldehyde (69% yield). 4,4′-Diiododiphenylmethane (**12**) was synthesized by diazotization of 4,4′-diaminodiphenylmethane followed by treatment with potassium iodide (41% yield). *N*-Phenylbenzimidoyl chloride (**13**) was prepared by literature procedure[47] (88% yield).

3-[(Trimethylsilyl)ethynyl]benzaldehyde and 3-Ethynylbenzaldehyde. A turbid solution of 107 g (0.578 mol) of 3-bromobenzaldehyde, 92.0 g (0.939 mol) of ethynyltrimethylsilane, 1.5 g of palladium(II) acetate, and 3.0 g of triphenylphosphine in 500 mL of deaerated, anhydrous triethylamine was rapidly heated to gentle reflux under argon. At ca. 100 °C, a clear yellow solution resulted, and a white precipitate began to form after 15 min at reflux. After 4 h, the mixture was cooled and the crystalline white solid of triethylamine hydrobromide was isolated by filtration; 105 g (0.577 mol, 99.8%). The orange-brown filtrate was concentrated, mixed with 500 mL of aqueous sodium bicarbonate, and extracted with dichloromethane (3 × 300 mL). The organic fractions were combined, dried over magnesium sulfate, and concentrated to yield an oil which was purified by distillation to yield analytically pure 3-[(trimethylsilyl)-ethynyl]benzaldehyde: 93.5 g (0.463 mol, 80.2%); bp 120–122 °C (0.15 torr); IR (film) 2958 (m, sharp, SiC–H), 2825 (m, sharp, H–CO), 2146 (m, sharp, C≡C), 1692 (vs, br, C=O), 1244 (s, sharp, Si–C), 843 cm^{-1} (s, br, Si–C bending); mass spectrum (70 eV), *m/e* (relative intensity) 202 (16.4, M$^{+\cdot}$), 187 (100, M$^{+\cdot}$ – CH$_3$); NMR (CDCl$_3$) δ 0.22 (s, 9 H, SiCH$_3$), 7.15–9.93 (m, 4 H, aromatic), 9.85 (s, 1 H, CHO).

Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.24; H, 6.97; Si, 13.88. Found: C, 71.10; H, 7.07; Si, 14.04.

3-[(Trimethylsilyl)ethynyl]benzaldehyde (16 g) prepared above was treated with 1 g of anhydrous potassium carbonate in 200 mL of methanol under argon at 25 °C for 3 h. The solvent was evaporated, and the residue was mixed with 100 mL of aqueous sodium bicarbonate and extracted with dichloromethane (3 × 50 mL). The combined organic fractions were dried over magnesium sulfate and concentrated to yield a yellow solid mass (crude yield 9.90 g, 76.2 mmol, 96.2%).

Purification of 5.0 g of the product by steam distillation yielded 2.60 g (62.0%) of a white flaky solid which was recrystallized from cold hexane to give lustrous white crystals of 3-ethynylbenzaldehyde: mp 76–76.5 °C; IR (KBr) 3240 (m, sharp, C≡CH), 2860, 2740 (w, sharp, O=CH), 2100 (w, sharp, C≡C); mass spectrum (70 eV), *m/e* (relative intensity) 130 (100, M$^{+\cdot}$), 129 (90.7, M$^{+\cdot}$ – H), 101 (60.7, M$^{+\cdot}$ – CHO); NMR (CDCl$_3$) δ 3.12 (s, 1 H, C≡CH), 7.16–8.00 (m, 4 H, aromatic), 9.85 (s, 1 H, CHO).

Anal. Calcd for C_9H_6O: C, 83.06; H, 4.65. Found: C, 83.06; H, 4.78.

Purification of a 4.90-g sample of the crude solid mass by column chromatography through silica gel gave 4.10 g (83.7%) of crystalline product, mp 75–76 °C.

4-[(Trimethylsilyl)ethynyl]benzaldehyde and 4-Ethynylbenzaldehyde. A deaerated solution of 24.5 g (132 mmol) of 4-bromobenzaldehyde and 1.0 g of triphenylphosphine in 300 mL of anhydrous triethylamine was treated with 20.0 g (204 mmol) of ethynyltrimethylsilane and then 0.3 g of palladium(II) acetate under argon. The mixture was heated at reflux for 2 h, cooled, and filtered to give 24.0 g (100%) of triethylamine hydrobromide. The filtrate was concentrated to a thick oil which solidified into long needles. The crude material was dissolved in hexane and filtered through silica gel to give 26.3 g (130 mmol, 98.6%) of 4-[(trimethylsilyl)ethynyl]benzaldehyde. An analytical sample was obtained by sublimation: mp 66–67 °C; IR (KBr) 2960 (m, sharp, SiCH), 2825, 2720 (m, sharp, HC=O), 2145 (m, sharp, C≡C), 1690 (vs, br, C=C), 1245 (s, sharp, SiC), 840 cm^{-1} (s, br, SiC); mass spectrum (70 eV), *m/e* (relative intensity) 202 (15.3, M$^{+\cdot}$), 187 (100, M$^{+\cdot}$ – CH$_3$); NMR (CDCl$_3$) δ 0.21 (s, 9 H, SiCH$_3$),

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7.60 (q, 4 H, J = 7.0 Hz, aromatic), 9.85 (s, 1 H, CHO).

Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.23; H, 7.33; Si, 13.88. Found: C, 71.31; H, 7.42; Si, 14.01.

4-[(Trimethylsilyl)ethynyl]benzaldehyde (16 g) was treated with 1.0 g of potassium carbonate in 50 mL of methanol under argon at 25 °C for 2 h. The solvent was removed, and 100 mL of dichloromethane was added. The solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated to yield 10.3 g of a yellow solid mass (crude yield 100%) which was purified by sublimation at 80–90 °C (0.025–0.25 torr): mp 88–90 °C; IR (KBr) 3240 (m, sharp, C≡CH), 2860, 2740 (w, sharp, O=CH), 2100 (w, sharp, C≡C), 1690 (s, br, C=O), 1590 cm^{-1} (m, sharp, C=C); mass spectrum (70 eV), m/e (relative intensity) 130 (100, $M^{+}\cdot$), 129 (90.7 $M^{+}\cdot$ – H), 101 (59.0, $M^{+}\cdot$ – CHO); NMR ($CDCl_3$) δ 3.21 (s, 1 H, C≡CH), 7.62 (distorted q, 4 H, aromatic), 9.88 (s, 1 H, CHO).

Anal. Calcd for C_9H_6O: C, 83.06; H, 4.65. Found: C, 82.90; H, 4.66.

2-[(Trimethylsilyl)ethynyl]benzaldehyde and 2-Ethynylbenzaldehyde.[48] A deaerated solution of 18.5 g (100 mmol) of 2-bromobenzaldehyde, 400 mg of triphenylphosphine, and 200 mg of palladium(II) acetate in 300 mL of anhydrous triethylamine was treated with 15.0 g (153 mmol) of ethynyltrimethylsilane under argon. The mixture was rapidly heated to ca. 80 °C and maintained at that temperature for 5 h. After cooling, the mixture was filtered to give 18.1 g (99.5 mmol, 99.5%) of triethylamine hydrobromide. The dark brown filtrate was concentrated, mixed with 100 mL of water, and extracted with dichloromethane (3 × 50 mL). The combined organic phases were dried, concentrated, and distilled at 108 °C (2 torr) to give 2-[(trimethylsilyl)ethynyl]benzaldehyde. An analytical sample was prepared by sublimation at 80–90 °C (0.1 torr): 15.2 g (75.2 mmol, 75%); mp 51–53 °C; IR (KBr) 2970 (w, sharp, $SiCH_3$), 2850, 2750 (w, sharp, O=CH), 2160 (m, sharp, C≡C), 1700 (s, sharp, C=O), 1595 (s, sharp, C=O), 1250 (s, sharp, SiC), 870, 845 cm^{-1} (s, br, SiC); mass spectrum (70 eV), m/e (relative intensity) 202 (14.2, $M^{+}\cdot$), 188 (100%, $M^{+}\cdot$ – CH_4), 128 (20.2, $M^{+}\cdot$ – $HSiMe_3$); NMR ($CDCl_3$) δ 0.09 (s, 9 H, $SiCH_3$), 7.00–7.77 (m, 4 H, aromatic), 10.27 (s, 1 H, CHO).

Anal. Calcd for $C_{12}H_{14}OSi$: C, 71.23; H, 7.33; Si, 13.88. Found: C, 71.19; H, 7.26; Si, 13.71.

The above product (15.2 g, 75.2 mol) was treated with 1 g of anhydrous potassium carbonate in 100 mL of methanol under argon at 25 °C for 5 h. The solvent was removed, and 100 mL of dichloromethane was added. The cloudy solution was washed with 100 mL of aqueous sodium bicarbonate, dried over magnesium sulate, and concentrated to yield 10.0 g of a yellow solid mass which was purified by sublimation at 0.025 torr: mp 60–61 °C (lit.[48] mp 60–60.5 °C); mass spectrum (70 eV), m/e (relative intensity) 130 (100, $M^{+}\cdot$), 129 (12.6, $M^{+}\cdot$ – H), 102 (98.4, $M^{+}\cdot$ – CO), 101 (35.5, $M^{+}\cdot$ – CHO); NMR ($CDCl_3$) δ 3.45 (s, 1 H, C≡CH), 7.20–7.70 (m, 4 H, aromatic), 10.15 (s, 1 H, CHO).

Methyl 3-[(Trimethylsilyl)ethynyl]benzoate and Methyl 3-Ethynylbenzoate. A deaerated solution of 26.5 g (123 mmol) of methyl 3-bromobenzoate, 200 mg of palladium(II) acetate, and 400 mg of triphenylphosphine in 300 mL of anhydrous triethylamine was treated with 20.0 g (204 mmol) of ethynyltrimethylsilane under argon. The pale yellow mixture was heated to 100 °C over 20 min and kept at 100 °C for 16 h. After cooling, the mixture was filtered to give 21.9 g (120 mmol, 97.8%) of triethylamine hydrobromide. The filtrate was concentrated, mixed with 300 mL of 5% hydrochloric acid, and extracted with dichloromethane (2 × 300 mL). The combined organic extracts were dried over magnesium sulfate, concentrated, and distilled at 79–85 °C (0.001 torr) to yield 19.5 g (84.0 mmol, 70.0%) of methyl 3-[(trimethylsilyl)ethynyl]benzoate: IR (film) 2970 (m, sharp, SiCH), 2160 (m, sharp, C≡C), 1720 (vs, sharp, C=O), 1290 (s, br, O), 1250 (m, sharp, SiC), 840 cm^{-1} (vs, br, SiC bending); mass spectrum (70 eV), m/e 232 ($M^{+}\cdot$).

The compound prepared above (8.20 g, 35.3 mmol) was mixed with 0.5 g of anhydrous potassium carbonate in 100 mL of methanol at 25 °C under argon. The mixture was stirred for 3 h. After solvent removal, the residue was dissolved in 100 mL of dichloromethane, washed with 100 mL each of aqueous sodium bicarbonate and water, and dried over magnesium sulfate. The solution was concentrated to an oil which solidified on standing. Sublimation at 47 °C (0.005 torr) afforded 4.00 g (25.0 mmol, 70.8%) of white crystals: mp 48–50 °C; IR (film) 3305 (s, sharp, C≡CH), 2960 (m, sharp, CH), 2120 (w, sharp, CC), 1735 (vs, br, C=O), 1300 cm^{-1} (vs, br, O); mass spectrum (70 eV), m/e (relative intensity) 160 ($M^{+}\cdot$); NMR ($CDCl_3$) δ 3.10 (s, 1 H, C≡CH), 3.91 (s, 3 H, CO_2CH_3), 7.33–8.17 (m, 4 H, aromatic).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.77; H, 5.34.

Methyl 4-[(Trimethylsilyl)ethynyl]benzoate and Methyl 4-Ethynylbenzoate. A deaerated solution of 21.5 g (100 mmol) of methyl 4-bromobenzoate, 200 mg of palladium(II) acetate, and 400 mg of triphenylphosphine in 300 mL of anhydrous triethylamine was treated with 20.0 g (204 mmol) of ethynyltrimethylsilane, heated to 100 °C over 30 min, and kept at 100 °C for 4 h. After cooling, the mixture was filtered to give 17.5 g (96.2 mol, 96.2%) of triethylamine hydrobromide. The filtrate was concentrated, mixed with 200 mL of 5% hydrochloric acid, and extracted with dichloromethane (3 × 100 mL). The combined organic fractions were dried over magnesium sulfate and concentrated to yield a solid mass which was purified by charcoal treatment and recrystallization from 100 mL of hexane: 16.0 g (69.0 mmol, 69.0%); mp 55–55.5 °C; IR (KBr) 2960 (m, sharp, SiCH), 2160 (m, sharp, C≡C), 1718 (s, sharp, C=O), 1597 (m, sharp, C=C), 1274 (strong, br, O), 1242 cm^{-1} (s, sharp, SiC); mass spectrum (70 eV), m/e 232 ($M^{+}\cdot$); NMR ($CDCl_3$) δ 0.28 (s, 9 H, Si, CH_3), 3.90 (s, 3 H, CO_2CH_3), 7.52 and 8.00 (q, 4 H, J_{AB} = 8.0 Hz, aromatic).

The above product (15 g, 65.1 mmol) was mixed with 0.5 g of anhydrous potassium carbonate in 100 mL of methanol. The mixture was stirred for 3 h under argon at 25 °C. After solvent removal (water bath of the rotary evaporator should not exceed room temperature), the residue was dissolved in 100 mL of dichloromethane, and the mixture was washed with 100 mL each of aqueous sodium bicarbonate and water, dried over magnesium sulfate, and concentrated to an oil which slowly solidified. Sublimation at 60 °C (2.5 torr) yielded 7.50 g (46.9 mmol, 73.1%) of methyl 4-ethynylbenzoate: mp 92.5–93.5 °C; IR (KBr) 3226 (s, sharp, C≡CH), 2092 (w, sharp, C≡C), 1695 (vs, vbr, C=O), 1595 (s, sharp, C=C), 1274 cm^{-1} (vs, vbr, ester O); mass spectrum (70 eV), m/e 160 ($M^{+}\cdot$); NMR ($CDCl_3$) δ 3.19 (s, 1 H, C≡CH), 3.88 (s, 3 H, CO_2CH_3), 7.70 (q, 4 H, J_{AB} = 8.0 Hz, aromatic).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 75.11; H, 5.16.

3-[(Trimethylsilyl)ethynyl]benzotrifluoride and 3-Ethynylbenzotrifluoride. A deaerated solution of 22.5 g (0.100 mol) of 3-bromobenzotrifluoride and 10.8 g (0.110 mol) of ethynyltrimethylsilane in 300 mL of anhydrous triethylamine was treated with 100 mg of palladium(II) acetate, 0.5 g of triphenylphosphine, and 100 mg of copper(I) iodide. The mixture was heated to 80 °C over 30 min and kept at this temperature for 16 h. After the mixture cooled, the white precipitate of triethylamine hydrobromide was filtered off. A quantitative yield was realized. The filtrate was concentrated to a thick oil, dissolved in 200 mL of ether, and washed in succession with 200 mL each of 10% aqueous hydrochloric acid, water, saturated sodium bicarbonate, and water again. The organic phase was dried over magnesium sulfate, passed through a bed of silica gel, and concentrated to a yellow oil. Purification by distillation at 50–52 °C (0.05 torr) yielded 16.2 g (66.9 mmol, 66.9%) of 3-[(trimethylsilyl)ethynyl]benzotrifluoride: IR (neat) 2980 (m, sharp, $SiCH_3$), 2180 (m, sharp, C≡C), 1340 (s, sharp), 1250 (s, sharp, SiC), 1140, 1170 cm^{-1} (s, br, CF_3); mass spectrum, (70 eV) m/e (relative intensity) 242 (25, $M^{+}\cdot$), 227 (100, $M^{+}\cdot$ – 15); NMR ($CDCl_3$) δ 0.28 (s, 9 H, $SiCH_3$), 7.35–7.82 (m, 4 H, aromatic).

Anal. Calcd for $C_{12}H_{13}F_3Si$: C, 59.48; H, 5.41; F, 23.52; Si, 11.59. Found: C, 59.63; H, 5.50; F, 22.77; Si, 11.83.

A solution of 10.0 g (41.3 mmol) of 3-[(trimethylsilyl)-ethynyl]benzotrifluoride in 100 mL of anhydrous methanol was deaerated and treated with 400 mg of anhydrous potassium carbonate. Upon being stirred, the solution became slightly turbid, and a gentle exotherm took place. After 1 h, the turbidity disappeared, and the clear solution was stirred at 25 °C for an

(48) 2-Ethynylbenzaldehyde was previously synthesized by an eight-step procedure. See J. Ojima, T. Yokomachi, and T. Yokoyama, *Chem. Lett.*, 633 (1972).

additional 16 h. The solvent was removed, and the residue was dissolved in water and extracted three times with 50-mL portions of ether. The combined ethereal extracts were dried over magnesium sulfate and concentrated by distillation at 760 torr through a 12-cm Vigreux column. The concentrate was carefully distilled at 27 °C (100 torr) [lit.[49] bp 141–145 °C (760 torr)] to yield 4.20 g (24.7 mmol, 59.8%) of colorless 3-ethynylbenzotrifluoride: IR (neat) 3300 (vs, sharp, C≡CH), 2120 (w, sharp, C≡C), 1490, 1435 (m, sharp, C=C), 1340, 1120, 1200 cm^{-1} (vb, vs, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 170 (100, molecular ion), 169 (20), 151 (25), 120 (14); NMR ($CDCl_3$) δ 3.05 (s, 1 H, C≡CH), 7.25–7.90 (m, 4 H, aromatic).

Anal. Calcd for $C_9H_5F_3$: C, 63.54; H, 2.96. Found: C, 63.58; H, 2.93.

1-Bromo-2-fluoro-5-nitrobenzene. To a solution of 35.0 g (200 mmol) of 1-bromo-2-fluorobenzene in 200 mL of concentrated sulfuric acid was added 16 mL of 69.8% nitric acid. The temperature of the mixture was maintained below 40 °C. After the addition was complete, the mixture was stirred at 20 °C for 16 h, diluted with 1 L of ice–water, and filtered. The solid was recrystallized from hexane to give a quantitative yield of a crystalline product: mp 55 °C; IR and NMR spectra were superimposable with those of an authentic sample of 1-bromo-2-fluoro-5-nitrobenzene prepared by a literature method.[43]

3-Bromo-4-fluoroaniline. A mixture of 10.0 g (45.4 mmol) of 1-bromo-2-fluoro-5-nitrobenzene and 30 g of iron filings (40 mesh) in 150 mL of methanol was heated at reflux for 16 h. The mixture was filtered through silica gel, concentrated, mixed with water, basified to pH 8, and then extracted with ether (3 × 200 mL). The combined ethereal extracts were dried over magnesium sulfate and concentrated to a brown oil. Distillation at 76–78 °C (0.35 torr) gave 5.50 g (28.9 mmol, 63.8%) of a colorless liquid which solidified upon standing: IR (neat film) 3460, 3360, 3220 (m, br, NH_2), 1620 (s, br, C≡C), 1500 cm^{-1} (s, sharp, C=C); mass spectrum (70 eV), *m/e* 191, 189 ($M^{+\cdot}$, Br present); NMR ($CDCl_3$) δ 3.60 (br s, 2 H, NH_2), 6.20–7.10 (m, 3 H, aromatic).

Anal. Calcd for C_6H_5BrFN: C, 37.93; H, 2.65; F, 10.00. Found: C, 38.04; H, 2.58; F, 9.95.

Impure 3-Ethynyl-4-fluoroaniline from 3-Bromo-4-fluoroaniline. A mixture of 10.0 g (52.6 mmol) of 3-bromo-4-fluoroaniline, 10.0 g (102 mmol) of ethynyltrimethylsilane, 300 mg of tris(2-tolyl)phosphine, and 150 mg of palladium(II) acetate was prepared in 100 mL of deaerated anhydrous triethylamine at 30–40 °C and then heated under argon at 90–100 °C for 22 h. The mixture was cooled and filtered to give 6.0 g (33 mmol, 62.6%) of the amine hydrobromide. The filtrate was concentrated and recycled with fresh catalyst. At the end, a total of 6.20 g (34.1 mmol, 64.8%) of the amine hydrobromide was obtained. The black oil was distilled at 80–90 °C (0.15 torr) to give a viscous yellow oil. The product above was treated with 100 mg of potassium carbonate in 50 mL of methanol at 25 °C for 16 h. After solvent removal, the residue was dissolved in ether and washed with 100 mL of water. The ethereal fraction was dried over magnesium sulfate and concentrated to an oil, which was purified by column chromatography. The NMR spectrum of the isolated end product (4.7 g) showed that it was a mixture of 40% 3-bromo-4-fluoroaniline and 60% 3-ethynyl-4-fluoroaniline.

2-Fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene. A mixture of 22.0 g (100 mmol) of 1-bromo-2-fluoro-5-nitrobenzene, 15.0 g (153 mmol) of ethynyltrimethylsilane, 1 g of triphenylphosphine, and 0.5 g of palladium(II) acetate in 250 mL of deaerated triethylamine was heated at 100 °C for 24 h under argon. The cooled mixture was filtered to remove 18.3 g (100%) of triethylamine hydrobromide. The filtrate was concentrated to a dark brown oil which, on distillation at 110–115 °C (0.3 torr), gave 18.5 g (78.1 mmol, 78.1%) of a yellow oil which was identified as 2-fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene: IR (neat) 2960 (m, sharp, SiCH), 1520, 1350 (s, br, NO_2), 1250 (s, sharp, SiC), 840 cm^{-1} (vs, br, SiC bending); mass spectrum (70 eV), *m/e* 237 (molecular ion); NMR ($CDCl_3$) δ 0.30 (s, 9 H, $SiCH_3$), 7.22 (t, 1 H, J = 8.0 Hz, aromatic H_6), 8.00–8.50 (m, 2 H, aromatic).

1-Ethynyl-2-methoxy-5-nitrobenzene. To a slurry of 1 g of potassium carbonate in 100 mL of methanol was added 18.5 g (78.1 mmol) of 2-fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene. An exothermic reaction ensued. The solution was stirred at 25 °C for 2 h. A copious precipitate was obtained at the end of the reaction period. The solvent was removed, and the residue was dissolved in 100 mL of dichloromethane and washed with 100 mL each of water, 10% hydrochloric acid, and then water. The organic phase was dried over magnesium sulfate and concentrated to a semisolid which yielded a yellow crystalline solid upon trituration with hexane, 6.60 g (40.0 mmol, 51.2%). This product was identified as 1-ethynyl-2-methoxy-5-nitrobenzene: IR (KBr) 3300 (s, sharp, C≡CH), 2120 (w, sharp, C≡C), 1610, 1580 (s, sharp, C=C), 1520, 1350 (s, br, NO_2), 1280 cm^{-1} (s, sharp, COC); mass spectrum (70 eV), *m/e* 165 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 3.28 (s, 1 H, C≡CH), 3.90 (s, 3 H, OCH_3), 6.82 (d, 1 H, J = 8.0 Hz, aromatic H_6), 8.10–8.30 (s and d, 2 H, aromatic).

Anal. Calcd for $C_9H_7NO_3$: C, 61.02; H, 3.98; N, 7.91. Found: C, 61.22; H, 3.92; N, 7.98.

3-Ethynyl-4-fluoroaniline from 2-Fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene. In 50 mL of methanol were mixed 5.00 g (21.1 mmol) of 2-fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene and 5 g of iron filings (40 mesh). Enough concentrated hydrochloric acid was added to render the medium acidic (pH 4–5). The mixture was heated at reflux for 16 h, cooled, and filtered through silica gel. The filtrate was concentrated to yield a massive solid residue which was then thoroughly extracted with ether. The ethereal extracts were combined and concentrated. The oily residue was distilled at 106–108 °C (0.2 torr) to give 2.30 g (11.1 mmol, 52.6%) of a pale yellow oil, identified as 4-fluoro-3-[(trimethylsilyl)ethynyl]aniline: IR (film) 3470, 3380, 3220 (m, br, NH_2), 2960 (s, sharp, SiCH), 2900 (w, sharp, CH), 2160 (s, sharp, C≡C), 1620, 1500 (s, br), 1250 (s, br, SiC), 1220 (s, br), 840 cm^{-1} (s, vbr, SiC bending); NMR ($CDCl_3$) δ 0.30 (s, 9 H, $SiCH_3$), 3.50 (br, 2 H, NH_2), 6.20–7.00 (m, 3 H, aromatic).

The product was treated with 100 mg of potassium carbonate in 20 mL of methanol for 15 h. The solution was concentrated, diluted with 50 mL of water, brought to neutrality, and then extracted with ether (3 × 50 mL). The combined ethereal extracts were dried over magnesium sulfate, concentrated, and purified by distillation: IR (neat) 3320 (s, sharp, C≡CH), 3480, 3400, 3230 (s, br, NH_2), 2120 cm^{-1} (w, sharp, C≡C); mass spectrum (70 eV), *m/e* 135 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 3.25 (s, 1 H, C≡CH), 3.60 (br s, 2 H, NH_2), 6.20–7.40 (m, 3 H, aromatic).

6-(3-Bromophenyl)benzimidazoquinazoline. A slurry of 4.18 g (20.0 mmol) of 2-(2-aminophenyl)benzimidazole and 4.07 g (22.0 mmol) of 3-bromobenzaldehyde in 30 mL of deaerated nitrobenzene was stirred at 25 °C to yield a copious pale yellow precipitate. The mixture was then heated to reflux under argon over 1 h and then at reflux for 19 h. Periodically, the system was vented to remove water vapor. The dark brown solution was cooled to 25 °C, and a white precipitate was obtained. The mixture was diluted with an equal volume of ether and filtered. The isolated white solid was washed with ether and air-dried, yielding 5.90 g (15.8 mmol, 78.9%) of product, mp 234–235 °C. Recrystallization from 1:1 dichloromethane–hexane raised the melting point to 237–238 °C: IR (KBr) 3030 (m, sharp, CH), 1613, 1580 (s, sharp, C=N), 1550, 1517, 1470, 1453, 1437, 1353, 1332 cm^{-1} (s, sharp, aromatic C=C); mass spectrum (70 eV), *m/e* (relative intensity) 375, 373 (100, $M^{+\cdot}$) 294 (20.8, $M^{+\cdot}$ – Br); NMR ($CDCl_3$) δ 6.50–8.28 (m, aromatic).

Anal. Calcd for $C_{20}H_{12}N_3Br$: C, 64.19; H, 3.23; N, 11.23; Br, 21.35. Found: C, 64.14; H, 3.30; N, 11.11; Br, 21.46.

6-[3-[(Trimethylsilyl)ethynyl]phenyl]benzimidazoquinazoline and 6-(3-Ethynylphenyl)benzimidazoquinazoline. A deaerated slurry of 3.00 g (8.02 mmol) of 6-(3-bromophenyl)benzimidazoquinazoline, 100 mg of palladium(II) acetate, and 200 mg of triphenylphosphine in 150 mL of 2:1 triethylamine–toluene was heated to 100 °C under argon and then treated by dropwise addition with 1.57 g (16.0 mmol) of ethynyltrimethylsilane. After 15 min, the initially white slurry darkened and became a clear solution. After 1 h, precipitation began to take place. The mixture was cooled after a total of 3.5 h and filtered to yield 1.20 g (65.9 mmol, 82.2%) of triethylamine hydrobromide. The filtrate was diluted with 100 mL of ether, washed with 200 mL each of 5% hydrochloric acid and water, and dried over magnesium sulfate. The solution was concentrated to give a solid mass which was recrystallized from hexane: 2.21

(49) M. Schlosser and V. Landenberger, *Chem. Ber.*, **100**, 3901 (1967). The yield was not specified in this reference.

g (5.65 mmol, 70.5%); IR (KBr) 3077 (m, sharp, CH), 2960 (m, sharp, SiCH), 2155 (s, sharp, C≡C), 1621, 1587 (vs, sharp, C=N), 1524, 1456, 1441, 1355, 1325 (s, sharp, C=C), 1247 (vs, sharp, SiC), 844 cm^{-1} (vs, br, SiC bending); mass spectrum (70 eV), m/e 391 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 0.30 (s, 9 H, $SiCH_3$), 7.00–8.00 (m, 12 H, aromatic).

A slurry of 2.00 g (51.2 mmol) of 6-[3-[(trimethylsilyl)-ethynyl]phenyl]benzimidazoquinazoline and 200 mg of anhydrous potassium carbonate in 100 mL of methanol was stirred at 25 °C for 3 h. The solvent was removed, the residue dissolved in 50 mL of chloroform, and the mixture washed with 50 mL each of 5% hydrochloric acid and water. Subsequent drying, concentrating, and recrystallization of the concentrate from 50 mL of 1:1 ether–hexane yielded 1.55 g (4.86 mmol, 94.9%) of 6-(3-ethynylphenyl)benzimidazoquinazoline: mp 170–178 °C (melted and resolidified); IR (KBr) 3300 cm^{-1} (m, sharp, C≡CH); mass spectrum (70 eV), m/e 319 ($M^{+\cdot}$); NMR ($CDCl_3$) acetylene proton at δ 3.17.

2-(2-Amino-5-bromophenyl)benzimidazole. A brown solution of 10.0 g (47.9 mmol) of 2-(2-aminophenyl)benzimidazole in 100 mL of glacial acetic acid at 0 °C was treated by dropwise addition with 7.66 g (47.9 mmol) of bromine in 25 mL of glacial acetic acid. The discharge of the bromine color was instantaneous. After complete addition, a precipitate appeared. The mixture was stirred at 25 °C for 30 min, diluted with twice its volume of water, and then treated with a 40% aqueous sodium hydroxide solution until basic (ca. pH 8–9). The granular precipitate was isolated by filtration, washing with a 1:1 water–methanol solution and hexane, and finally air-drying. The yield was 12.5 g (43.4 mmol, 90.6%): mp 236–239 °C; IR (KBr) 3225 (s, br, NH), 1600, 1590 (m, sharp, C=N), 1515, 1479, 1410, 1239 (all ms, sharp, C=C), 866 cm^{-1} (m, br, CBr); mass spectrum (70 eV), m/e (relative intensity) 289, 287 (100, $M^{+\cdot}$), 208 (28.4, $M^{+\cdot}$ – Br).

10-Bromo-6-(3-bromophenyl)benzimidazoquinazoline. A slurry of 19.0 g (34.7 mmol) of 2-(2-amino-5-bromophenyl)-benzimidazole and 7.20 g (38.9 mmol) of 3-bromobenzaldehyde in 100 mL of deaerated nitrobenzene was stirred at 25 °C for 15 min. The yellow suspension slowly dissolved to give a yellow-brown solution, which immediately yielded a copious yellow precipitate. The mixture was heated under argon to a gentle reflux over 45 min. The red-brown solution was stirred under argon at reflux for 20 h. The course of the reaction was monitored by thin-layer chromatography on silica gel plates.

The mixture was cooled to 25 °C, mixed with twice its volume of ether, and filtered to yield an off-white powdery solid which was thoroughly washed with ether and hexane: 10.9 g (24.1 mmol, 69.3%); mp 272–273 °C; IR (KBr) 3077 (w, br, CH), 1621, 1587, 1524, 1471, 1458, 1445, 1425, 1355 (all m, sharp), 823 cm^{-1} (vbr, s); mass spectrum (70 eV), m/e (relative intensity) 453 (100, $M^{+\cdot}$), 374 (10.4, $M^{+\cdot}$ – Br), 293 (10.4, $M^{+\cdot}$ – 2Br).

10-[(Trimethylsilyl)ethynyl]-6-[3-[(trimethylsilyl)-ethynyl]phenyl]benzimidazoquinazoline and 10-Ethynyl-6-(3-ethynylphenyl)benzimidazoquinazoline. A slurry of 10.0 g (22.1 mmol) of 10-bromo-6-(3-bromophenyl)benzimidazoquinazoline in 400 mL of a 1:1 triethylamine–toluene mixture was deaerated and heated to 100 °C under argon. The solid did not dissolve completely. The catalyst (500 mg of triphenylphosphine and 250 mg of palladium(II) acetate) was introduced, and the entire mixture was treated by dropwise addition with 10.0 g (102 mmol) of ethynyltrimethylsilane. After 30 min more solids appeared to have dissolved, and the supernatant solution acquired an orange tint. As the reaction progressed, the solution slowly turned greenish brown, and the precipitate that was visible had a different texture. After 4 h thin-layer chromatography (silica gel) of the reaction mixture revealed the absence of starting material and the presence of a highly fluorescent material as product. The reaction mixture was cooled and filtered to yield 7.80 g (42.9 mmol, 97.0%) of triethylamine hydrobromide. The filtrate was concentrated, and the solid residue was dissolved in 100 mL of ether and washed in succession with 100 mL of 10% hydrochloric acid, 100 mL of saturated sodium bicarbonate, and 100 mL of water. After being dried over magnesium sulfate, the ethereal solution was concentrated to yield a pale yellow solid mass which was washed with 100 mL of hexane and air-dried. The yield was 8.20 g (16.8 mmol, 76.2%): mp 245–246.5 °C; IR (KBr) 2959 (s, sharp, SiCH), 2155 (s, sharp, C≡C), 1618, 1587 (s, sharp, C=N), 1497, 1473, 1445, 1408, 1355 (all s and sharp, C=C), 1247 cm^{-1} (vs, sharp, SiC); mass spectrum (70 eV), m/e (relative intensity) 489 (100, $M^{+\cdot}$ + 2 H), 473 (51.4, $M^{+\cdot}$ + 2 H – CH_4); NMR ($CDCl_3$) δ 0.27, 0.48 (2 s, 18 H, $SiCH_3$), 7.30–8.00 (m, 12 H, aromatic).

A slurry of 7.50 g (15.4 mmol) of 10-[(trimethylsilyl)-ethynyl]-6-[3-[(trimethylsilyl)ethynyl]phenyl]benzimidazoquinazoline and 1.0 g of anhydrous potassium carbonate in 150 mL of a 2:1 methanol–toluene mixture was stirred under argon at 25 °C. After 15 min, the solids dissolved to yield a dark brown solution. Complete disappearance of the starting material was effected in 45 min, as revealed by thin-layer chromatography. The solvents were removed, and the yellow residue was dissolved in 200 mL of dichloromethane, washed with 200 mL of 5% hydrochloric acid, and dried over magnesium sulfate. Removal of solvent gave a pale yellow powdery solid: 5.30 g (15.4 mmol, 100%); mp >220 °C; IR (KBr) 3500–3000 (br, s, hydrate), 3300 (s, sharp, C≡CH), 2110 (w, sharp, C≡C), 1625, 1590 (s, sharp, C=N), 1530, 1480, 1450, 1420, 1360, 1330 cm^{-1} (s, sharp); mass spectrum (70 eV), m/e (relative intensity) 343 (100, $M^{+\cdot}$), no other significant peaks; NMR ($CDCl_3$) δ 3.17, 3.27 (2 s, 2 H, C≡CH), 7.30–8.10 (m, 11 H, aromatic). An analytical sample was prepared by column chromatography (silica gel, 1:1 dichloromethane–hexane).

Anal. Calcd for $C_{24}H_{13}N_3 \cdot 1.5H_2O$: C, 77.82; H, 4.35; N, 11.34. Found: C, 77.56; H, 3.92; N, 11.02.

4-[4-[(Trimethylsilyl)ethynyl]phenoxy]benzil and 4-(4-Ethynylphenoxy)benzil. A mixture of 3.80 g (9.97 mmol) of 4-(4-bromophenoxy)benzil, 100 mg of palladium(II) acetate, and 200 mg of tris(2-tolyl)phosphine in 100 mL of anhydrous triethylamine was deaerated and warmed to ca. 80 °C under argon. At this point, a clear yellow solution was obtained and was treated with 2.50 g (25.5 mmol) of ethynyltrimethylsilane. After being stirred at ca. 100 °C for 16 h, the mixture was cooled and filtered to remove the amine salt. The filtrate was concentrated, dissolved in 200 mL of ether, and extracted with 100 mL each of 5% hydrochloric acid and water. The ethereal solution was concentrated to a thick oil: 3.49 g (8.78 mmol, 88.0%); IR (neat) 2960 (m, sharp, $SiCH_3$), 2160 (m, sharp, C≡C), 1680 (s, br, C=O), 1590, 1585 (s, br, C=C), 1250, 1210 (vs, sharp, SiC and O), 840 cm^{-1} (vs, br, SiC bending); NMR ($CDCl_3$) δ 0.30 (s, 9 H, $SiCH_3$), 6.80–8.00 (3 distorted d, 13 H, aromatic).

The crude oil was dissolved in 100 mL of anhydrous methanol containing 20% anhydrous ether. About 100 mg of potassium carbonate was added, and the mixture was stirred under argon at 25 °C for 16 h. The brown solution was diluted with 500 mL of water and extracted with ether (3 × 150 mL). The combined ethereal extracts were dried over magnesium sulfate and concentrated to a brown oil which was purified by column chromatography through silica gel. The desired product was eluted with a 1:2 dichloromethane–hexane mixture. Evaporation of the solvent from the eluate yielded 1.60 g (4.91 mmol, 55.9%) of a viscous yellow oil: IR (film) 3300 (m, br, C≡CH), 2100 (w, sharp, C≡C), 1675 (s, br, C=O), 1590 (s, br, C=C), 1250 cm^{-1} (vs, vbr, ether O); mass spectrum (70 eV), m/e 326 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 3.10 (s, 1 H, C≡CH), 6.90–8.10 (3 distorted d, 13 H, aromatic).

A solid derivative of 4-(4-ethynylphenoxy)benzil was prepared as follows. The oily product (1.60 g, 4.91 mmol) was mixed with 0.55 g of *o*-phenylenediamine in 20 mL of ethanol and was heated to a gentle boil for 30 min. The resulting solution was cooled slowly to 25 °C and then placed at −78 °C to induce crystallization. The pale yellow crystalline product was further purified by column chromatography to yield a white crystalline solid: 1.60 g (4.02 mmol, 81.9%); mp 129–130 °C; IR (KBr) 3450 (br, m), 3279, 3226 (w, sharp, C≡CH), 1585, 1486 (m, sharp, C=N, C=C), 1235 cm^{-1} (s, br, O); NMR ($CDCl_3$) δ 3.00 (s, 1 H, C≡CH), 6.85–8.35 (m, 17 H, aromatic).

Anal. Calcd for $C_{28}H_{18}N_2O \cdot H_2O$: C, 80.75; H, 4.84; N, 6.73. Found: C, 80.64; H, 4.77; N, 6.73.

4,4′-Diiododiphenylmethane. A slurry of 17.0 g (85.9 mmol) of 4,4′-diaminodiphenylmethane in 300 mL of concentrated sulfuric acid was stirred at 25 °C until all solid particles dissolved. The dark brown solution was cooled to 0–5 °C while a 30-mL aqueous solution of 17.0 g (0.239 mol) of sodium nitrite was added dropwise. Care was taken not to let temperature rise above 5 °C. After the addition was completed, the slurry was stirred for 30 min at 5 °C and then slowly poured into an aqueous solution of

100 g of potassium iodide in 2 L of water preheated to 55 °C. The resulting mixture was stirred for 1 h at 55 °C, cooled to 25 °C, mixed with 1 L of dichloromethane, *neutralized* by the addition of 50% aqueous sodium hydroxide, and then decolorized with saturated aqueous sodium bisulfite solution. The brown organic phase was separated and washed with 500 mL each of 10% aqueous hydrochloric acid, distilled water, saturated aqueous sodium bicarbonate, and then water. After the mixture was dried over magnesium sulfate and concentrated, the crude oil was purified by column chromatography through silica gel by using hexane as eluant. The white crystalline solid was identified as 4,4′-diiododiphenylmethane: 15.0 g (35.7 mmol, 41.6%); mp 85–86 °C (lit. mp 89–91,[50] 92–93 °C[51]); IR (KBr) 2950 (w, sharp, CH), 1490, 1400 (s, sharp, C=C), 1020, 810, 780 cm^{-1} (s, sharp); NMR ($CDCl_3$) δ 3.83 (s, 2 H, CH_2), 6.87 and 7.60 (q, 8 H, J_{AB} = 8.0 Hz, aromatic).

Bis[4-[(trimethylsilyl)ethynyl]phenyl]methane. A solution of 8.40 g (20.0 mmol) of 4,4′-diiododiphenylmethane and 5.00 g (51.0 mmol) of ethynyltrimethylsilane in 150 mL of 2:1 triethylaminetoluene was deaerated with argon and treated with the catalyst mixture made up of 50 mg of palladium(II) acetate, 150 mg of triphenylphosphine, and 50 mg of copper(I) iodide. The yellow solution was stirred and warmed to 80–90 °C over 1 h and kept at this temperature range for 4 h. The copious white precipitate that was formed was filtered off after the mixture was cooled to 25 °C and diluted with 150 mL of ether. The yield of triethylamine hydroiodide was quantitative. The filtrate was concentrated to a thick oil, dissolved in 200 mL of ether, and washed with 200 mL each of 10% aqueous hydrochloric acid, water, saturated aqueous sodium bicarbonate, and water again. The ethereal phase was dried over magnesium sulfate and concentrated to an oil which crystallized on standing. The solid was taken up in 100 mL of 1:1 hexane–dichloromethane and filtered through a bed of silica gel. The filtrate was evaporated down to half of the original volume and cooled at −78 °C to precipitate 7.20 g (20.0 mmol, 100%) of a crystalline solid. Recrystallization from spectro-grade hexane yielded pure, lustrous crystals with 81% recovery: mp 110–111 °C; IR (KBr) 2970 (s, sharp, $SiCH_3$), 2160 (s, sharp, C≡C), 1505 (s, sharp, C=C), 1250 (s, sharp, $SiCH_3$), 840 cm^{-1} (vs, br, SiC bending); NMR ($CDCl_3$) δ 0.28 (s, 18 H, $SiCH_3$), 3.92 (s, 2 H, CH_2), 7.37 and 7.40 (q, 8 H, J_{AB} = 8.0 Hz, aromatic).

Anal. Calcd for $C_{23}H_{28}Si_2$: C, 76.60; H, 7.83; Si, 15.58. Found: C, 76.28; H, 7.84; Si, 15.84.

Bis(4-ethynylphenyl)methane. A suspension of 1.00 g (2.78 mmol) of bis[4-[(trimethylsilyl)ethynyl]phenyl]methane in 50 mL of anhydrous deaerated methanol was treated with enough anhydrous ether to dissolve all solid particles at 25 °C. Anhydrous potassium carbonate (300 mg) was added, and the mixture was stirred at 25 °C under argon for 16 h. The solvent was removed, and the solid residue was dissolved in 50 mL of dichloromethane, treated with 5 g of silica gel, and evaporated to dryness. The powder was placed on top of a 40-cm (30-mm i.d.) column of silica gel (EM Labs, 70–230 mesh), and the column was developed with spectro-grade hexane. Crystalline white solids were recovered from the eluate: 0.60 g (2.78 mmol, 100%); mp 63–64 °C. After the product was dried at 56 °C (0.01 torr) inside an Abderhalden apparatus for 2 h, the melting point rose to 65.5–66.5 °C: IR (KBr) 3280 (vs, sharp, C≡CH), 2100 (w, sharp, C≡C), 1500 cm^{-1} (m, sharp, C=C); mass spectrum (70 eV), m/e 216 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 3.03 (s, 2 H, C≡CH), 3.95 (s, 2 H, CH_2), 7.10 and 7.43 (q, 8 H, J_{AB} = 8.0 Hz, aromatic).

Anal. Calcd for $C_{17}H_{12}$: C, 94.41; H, 5.59. Found: C, 94.34; H, 5.70.

1-Phenyl-2-propyn-1-one Anil. *N*-Phenylbenzimidoyl chloride was prepared by a standard procedure[47] [90%, bp 120–125 °C (0.1 torr), mp 40–40.5 °C]. A solution of 21.5 g (0.100 mol) of *N*-phenylbenzimidoyl chloride in 250 mL of deaerated triethylamine was treated with 10.5 g of ethynyltrimethylsilane, with 0.1 g of palladium(II) acetate, and then with 0.2 g of triphenylphosphine. The mixture was slowly heated to 80 °C and kept at 80 °C for 2 h. After cooling, diluting with an equal volume of ether, and filtering, 10.5 g of triethylamine hydrochloride was isolated (98% of theory). The filtrate was concentrated and eluted through a short column of silica gel with hexane. The eluate was concentrated and distilled at 130–135 °C (0.1 torr) to yield a viscous yellow oil which was identified as 3-(trimethylsilyl)-1-phenyl-2-propyn-1-one anil: 21.7 g (78.3%); IR (film) 2960 (m, sharp, $SiCH_3$), 2160 (w, sharp, C≡C), 1590, 1560 (s, sharp, C=N and C=C), 1250 (s, sharp, SiC), 850 cm^{-1} (s, br, SiC bending); mass spectrum (70 eV), m/e 277 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 0.12 (s, 9 H, $SiCH_3$), 7.00–7.50 (m, 8 H, aromatic), 8.10–8.30 (m, 2 H, *o*-H on 1-phenyl).

To a solution of 1.50 g (5.42 mmol) of 3-(trimethylsilyl)-1-phenyl-2-propyn-1-one anil in 10 mL of anhydrous methanol was added 100 mg of anhydrous potassium carbonate. Immediately an exothermic reaction took place, and a copious crystalline precipitate was formed. The mixture was filtered and the crystalline pale yellow solid was washed with cold methanol: 1.00 g (4.88 mmol, 90.0%); mp 117–117.5 °C; IR (KBr) 3200 (s, sharp, C≡CH), 2080 (s, sharp, C≡C), 1590 and 1570 cm^{-1} (m, sharp, C=N and C=C); mass spectrum (70 eV), m/e 205 ($M^{+\cdot}$); NMR ($CDCl_3$) δ 3.28 (s, 1 H, C≡CH), 6.90–7.50 (m, 8 H, aromatic), 8.10–8.30 (m, 2 H, ortho H on 1-phenyl).

Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.81; H, 5.50; N, 6.83.

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Registry No. **1**, 3132-99-8; **2**, 1122-91-4; **3**, 6630-33-7; **4**, 618-89-3; **5**, 619-42-1; **6**, 401-78-5; **7**, 58534-94-4; **8**, 656-64-4; **9**, 77123-52-5; **10**, 77123-53-6; **11**, 77123-54-7; **12**, 23055-78-9; **13**, 4903-36-0; ethynyltrimethylsilane, 1066-54-2; palladium(II) acetate, 3375-31-3; 3-[(trimethylsilyl)ethynyl]benzaldehyde, 77123-55-8; 3-ethynylbenzaldehyde, 77123-56-9; 4-ethynylbenzaldehyde, 63697-96-1; 4-[(trimethylsilyl)ethynyl]benzaldehyde, 77123-57-0; 2-ethynylbenzaldehyde, 38846-64-9; 2-[(trimethylsilyl)ethynyl]benzaldehyde, 77123-58-1; methyl 3-ethynylbenzoate, 10602-06-9; methyl 3-[(trimethylsilyl)ethynyl]benzoate, 77123-59-2; methyl 4-[(trimethylsilyl)ethynyl]benzoate, 75867-41-3; methyl 4-ethynylbenzoate, 3034-86-4; 3-[(trimethylsilyl)ethynyl]benzotrifluoride, 40230-93-1; 3-ethynylbenzotrifluoride, 705-28-2; bis(4-ethynylphenyl)methane, 6140-83-6; 1-bromo-2-fluorobenzene, 1072-85-1; 1-phenyl-2-propyn-1-one anil, 15765-08-9; 3-ethynyl-4-fluoroaniline, 77123-60-5; 2-fluoro-5-nitro-1-[(trimethylsilyl)ethynyl]benzene, 77123-61-6; 1-ethynyl-2-methoxy-5-nitrobenzene, 77123-62-7; 4-(4-ethynylphenoxy)benzil, 61457-77-0; 4-fluoro-3-[(trimethylsilyl)ethynyl]aniline, 77123-63-8; 3-(trimethylsilyl)-1-phenyl-2-propyn-1-one anil, 77123-64-9; 2-(2-aminophenyl)benzimidazole, 5805-39-0; 4-(4-ethynylphenoxy)benzil *o*-phenylenediamine derivative, 61457-78-1; 4,4′-diaminodiphenylmethane, 101-77-9; 6-[3-[(trimethylsilyl)ethynyl]-phenyl]benzimidazoquinazoline, 77123-65-0; 6-(3-ethynylphenyl)-benzimidazoquinazoline, 77123-66-1; 2-(2-amino-5-bromophenyl)-benzimidazole, 77123-67-2; bis[4-(trimethylsilyl)ethynyl]phenyl]-methane, 77123-71-8; 10-[(trimethylsilyl)ethynyl]-6-[3-[(trimethylsilyl)ethynyl]phenyl]benzimidazoquinazoline, 77123-68-3; 10-ethynyl-6-(3-ethynylphenyl)benzimidazoquinazoline, 77123-69-4; 4-[4-[(trimethylsilyl)ethynyl]phenoxy]benzil, 77123-70-7.

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