chloride was removed by rotary evaporation, and CH_2Cl_2 (100 mL) was added. The solution was cooled to 0 °C, and a solution of tetra-*n*-butylammonium chloride (150 mg, 0.54 mmol) and sodium azide (4.50 g, 69.2 mmol) in 15 mL of water was added. The two-phase mixture was stirred for 3 h at 0 °C, the phases were separated, and the organic layer was washed with water (2 × 25 mL) and dried ($MgSO_4$). IR spectrum of this solution: 2190, 1715, 1565, 1420, 1360, and 1340 cm^{-1}. Trifluoroacetic acid (8.0 g, 70 mmol) was added, and the solution was filtered and refluxed for 18 h. The cooled mixture was washed with ice-cold 1 M $NaHCO_3$ solution (25 mL), dried ($MgSO_4$), and concentrated to afford a yellow solid. Ether was added (100 mL); the mixture was filtered and concentrated to give 11.3 g (84%) of *N*-(3,3-dinitrocyclobutyl)trifluoroacetamide: mp 82–84 °C; TLC (ether) R_f = 0.10; IR 3480, 3100, 1730, 1560, 1335, 1220, 1170 cm^{-1}; ^1H NMR δ 3.50 (m, 4 H), 4.52 (m, 1 H), 7.0 (br s, 1 H). Anal. Calcd for $C_6H_6F_3N_3O_5$: C, 28.03; H, 2.35; N, 16.34; F, 22.16. Found: C, 28.01; H, 2.56; N, 16.38; F, 22.14.

To a solution of above amide (11.3 g, 44.0 mmol) in 200 mL of methanol was added 20 mL of 12 M HCl. The solution was refluxed overnight and evaporated, and the residue was triturated with ether (2 × 40 mL) to give 8.70 g (100%) of **10**: mp 215–217 °C dec; IR (KBr) 3000, 1560, 1345 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.60 (m, 5 H), 8.50 (br s, 3 H). Anal. Calcd for $C_4H_8N_3ClO_4$: C, 24.32; H, 4.08; N, 21.27; Cl, 17.94. Found: C, 24.70; H, 4.26; N, 21.31; Cl, 17.56.

1,1,3,3-Tetranitrocyclobutane (8f) from 4f. A mixture of **4f** (50:50 cis/trans mixture) (0.42 g, 2.8 mmol), sodium carbonate (0.90 g, 8.5 mmol), and sodium nitrite (1.18 g, 17 mmol) was dissolved in water (25 mL) at 10 °C. After 20 min, the mixture was diluted with water (20 mL) and filtered, and ether (25 mL) was added. Then, a solution of silver nitrate (3.68 g, 21.7 mmol) in water (10 mL) was added, followed by a 10% NaOH solution (10 drops), and the mixture was stirred at 10 °C for 20 min and at room temperature for 20 min. The mixture was filtered through Celite. The aqueous layer was extracted with ether (3 × 40 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated to give 0.55 g of a mixture of 1,1,3-trinitrocyclobutane (**11**) and 1,1,3,3-tetranitrocyclobutane **8f** (2: 3 by ^1H NMR analysis). Recrystallization of this mixture from CH_2Cl_2–chloroform gave 0.25 g (38%) of **8f** as a colorless solid: mp 165–166 °C; d = 1.825 ($AgNO_3$ flotation); d = 1.83 (single-crystal X-ray[18]); IR 3000, 1595, 1400, 1365, 1330 cm^{-1}; NMR (acetone-d_6) δ 4.83 (s). Anal. Calcd for $C_4H_4N_4O_8$: exact mass (M′ – $2NO_2$), 144.0169; C, 20.35; H, 1.71. Found: exact mass, 144.0171; C, 20.47; H, 1.78.

8f from 7a. To a stirred solution of **7a** in 3:1 water–THF (140 mL) at 0 °C was added NaOH (2.70 g, 67.5 mmol). After 15 min, sodium nitrite (7.7 g, 0.11 mol) was added, and the mixture was stirred for 5 min. Ether (100 mL) and a solution of silver nitrate (19.0 g, 0.112 mol) in 100 mL of water were added, and the resulting mixture was stirred for 1 h at 0 °C and at ambient temperature for 2 h. Aqueous saturated NaCl (50 mL) was added, the suspension was filtered, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to give a semisolid. Repeated trituration with ether–hexanes and washing with cold anhydrous ether gave 1.14 g (21%) of **8f**: mp 165–166 °C, identical with that prepared above.

5,5,10,10-Tetranitrodispiro[3.1.3.1]decane (12). A mixture of 1 M aqueous NaOH (10 mL), dioxane (3 mL), and **4c** (0.20 g, 0.88 mmol) was stirred at 20 °C until it was homogeneous (15 min), and solid sodium nitrite (1.2 g, 17 mmol) was added. After 5 min, a mixture of sodium persulfate (1.26 g, 5.30 mmol) and potassium ferricyanide (0.35 g, 1.0 mmol) was added in one portion. The resulting red-amber solution was stirred at 20 °C for 3 h, and then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated to afford 0.21 g of a solid, which was sublimed (95 °C/0.10 mm) to give 0.10 g (64%) of **12**: mp 179–180 °C; IR 1575 cm^{-1}; NMR δ 2.20 (m, 4 H), 2.65 (m, 8 H); d = 1.52 g/cm^3; ($AgNO_3$ flotation). Anal. Calcd for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.82; N, 17.72. Found: C, 38.32; H, 3.84; N, 17.57.

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Registry No. **1d**, 120525-63-5; **2a**, 98431-84-6; **2b**, 100132-82-9; **2c**, 120525-64-6; **2d**, 120525-65-7; *cis*-**3a**, 120525-66-8; *trans*-**3a**, 120525-67-9; **3b**, 120525-68-0; **3c**, 120525-69-1; **3d**, 120525-70-4; *cis*-**4a**, 120525-71-5; *trans*-**4a**, 120525-72-6; **4b**, 120525-73-7; **4c**, 120525-74-8; **4d**, 120525-75-9; **4e**, 2625-41-4; *cis*-**4b**, 120525-76-0; *trans*-**4b**, 120525-77-1; *cis*-**5**, 120525-78-2; *trans*-**5**, 120525-79-3; **6a**, 29820-55-1; **6b**, 4935-01-7; *cis*-**7a**, 120525-80-6; *trans*-**7a**, 120525-81-7; *cis*-**7b**, 120525-82-8; *trans*-**7b**, 120525-83-9; **8a**, 120525-84-0; **8e**, 120525-85-1; **8f**, 120167-77-3; **9a**, 120167-76-2; **9b**, 120181-39-7; **10**, 120525-86-2; **11**, 120167-75-1; **12**, 120525-88-4; 3-methylenecyclobutanecarboxylic acid chloride, 98198-78-8; 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane, 120525-62-4; 1,3-diaminocyclobutane, 91301-66-5; *N*-(3,3-dinitrocyclobutyl)-trifluoroacetamide, 120525-87-3.

(18) X-ray structure of **8f** will published elsewhere. Gillardi, R. Naval Research Laboratory, private communication.

A New Method for Synthesis of Trifluoromethyl-Substituted Phenols and Anilines

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Triethyl(trifluoromethyl)silane and tri-*n*-butyl(trifluoromethyl)silane were found to react with quinones by addition to one of the carbonyl carbon atoms, giving dienones containing geminal trifluoromethyl and trialkylsiloxy substituents. These reactions were catalyzed by a variety of basic compounds. Quinones found to undergo this process include 1,2- and 1,4-benzoquinones (some bearing alkyl substituents), naphthoquinone, anthraquinone, and phenanthrenequinone. Most of the resulting dienones gave (trifluoromethyl)phenols on dissolving metal reduction, and one was subjected to reductive amination to give (trifluoromethyl)aniline.

The trifluoromethyl group is an increasingly popular aromatic substituent in compounds synthesized for biological applications. Still, only a handful of methods exist for its introduction into aromatic compounds. Classic methods such as conversion of methyl groups by photochlorination followed by hydrofluoric acid treatment[1] or

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Table I. Dienones Synthesized from Quinones, Et_3SiCF_3 (1) or $(n\text{-}Bu)_3SiCF_3$ (2), and Excess Potassium Fluoride

quinone	silane	solvent	product	yield, %
1,4-benzoquinone	1	CH_3CN	3	72
1,4-benzoquinone	2	CH_3CN	4	59
2,6-di-*tert*-butyl-1,4-benzoquinone	1	CH_3CN	5	70
3,5-di-*tert*-butyl-1,2-benzoquinone	1	CH_3CN	6	90
1,4-naphthoquinone	1	CH_3CN	7	44
9,10-anthraquinone	1	DMF	8	86
9,10-phenanthrenequinone	1	DMF	9	86

Scheme I

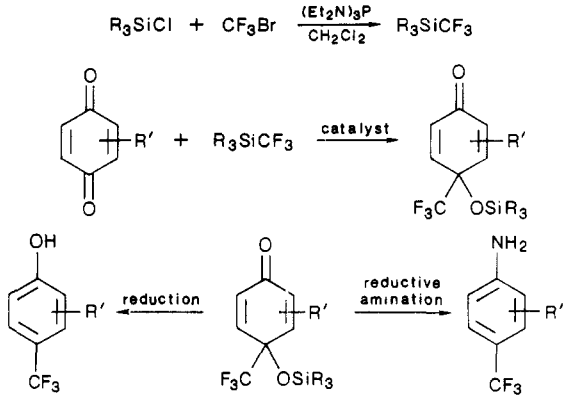
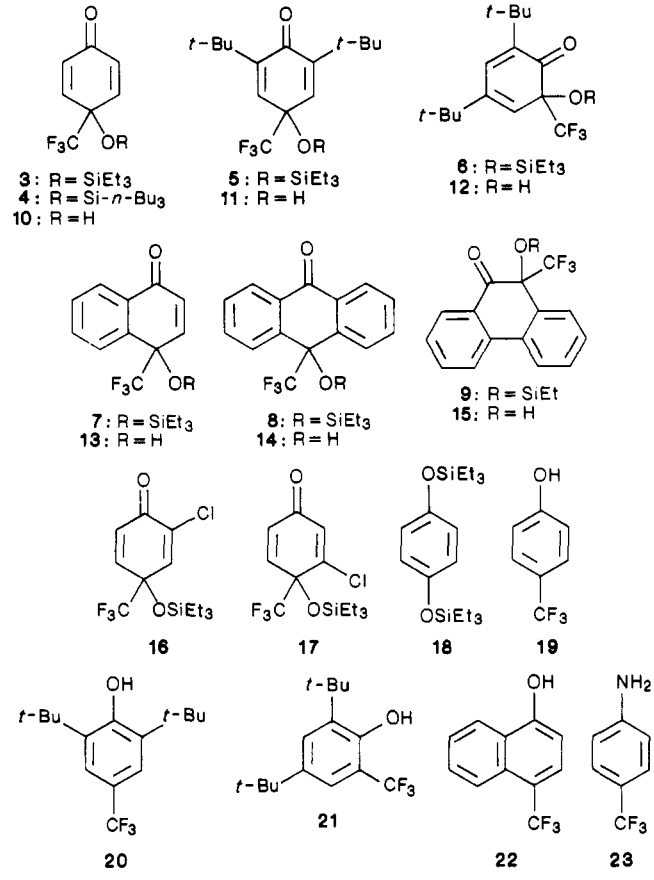


Chart I



conversion of acid groups using sulfur tetrafluoride[2] have been recently supplemented by several useful techniques. These include halogen displacement reactions[3-6] and direct introduction by either electrophilic[7,8] or radical[9,10] means. However, other aromatic substituents are not always well tolerated under the conditions of these methods, and consequently some types of trifluoromethylated aromatic compounds remain difficult to synthesize.

Two such classes of materials are (trifluoromethyl)-phenols and, to a lesser extent, anilines. Traditionally, the anilines have been synthesized from toluenes by (1) nitration, (2) photohalogenation, (3) halogen exchange using hydrogen fluoride, and (4) reduction. Diazotization followed by hydrolysis of the anilines gives the corresponding phenols.[11] Wakselman's use of bromotrifluoromethane to directly introduce the trifluoromethyl group into anilines is a vast improvement over the multistep procedure but suffers from the low positional selectivity common in homolytic aromatic substitutions.[9] The trifluoromethylation of aromatic compounds using carbon tetrachloride in hydrofluoric acid gives a 3:1 isomer mixture when applied to anisole and gives ethers when applied to phenol.[7,8]

We report herein a new method for synthesis of trifluoromethylated phenols and anilines that is short (three steps), convenient, and selective. It is based on the use of trialkyl(trifluoromethyl)silanes, which are readily synthesized from bromotrifluoromethane (Freon 13B1) by the method of Ruppert,[12] to transfer the trifluoromethyl group to either *o*- or *p*-quinones.[13] Reduction or reductive amination of the resulting dienones gives the desired aromatic compounds. The process is outlined in Scheme I.

Triethyl(trifluoromethyl)silane (1) and tri-*n*-butyl(trifluoromethyl)silane (2) were synthesized by the procedure shown in Scheme I in yields of 69 and 64%, respectively. Although the precursor chlorosilanes used to make 1 and 2 are more expensive than the methyl analogue (chlorotrimethylsilane), the higher boiling points of 1 and 2 relative to (trifluoromethyl)trimethylsilane (bp 45 °C)[12] made them more convenient to handle in the laboratory. Subsequent results (vide infra) indicated that the nature of the alkyl groups has little effect on the reactivity of compounds such as 1 and 2, at least in the systems we studied.

Quinones were found to react readily with 1 and potassium fluoride to give dienones as shown in Scheme I. A series of such dienones (compounds **3–9**, Chart I) were prepared by reaction of the requisite quinone, silane 1 or

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Table II. Catalysts for the Addition of Et_3SiCF_3 (1) or $(n\text{-}Bu)_3SiCF_3$ (2) to Quinones

quinone (mmol)	silane (mmol)	catalyst (mmol)[a]	solvent	temp, °C	time,[a] h	product	yield, %
1,4-benzoquinone (1.1)	1 (1.3)	CsF (1.1)	CH_3CN	25	on[b]	3	nd[c]
1,4-benzoquinone (1.1)	1 (1.3)	KHF_2 (1.3)	CH_3CN	25	2	3	42
1,4-benzoquinone (0.77)	1 (0.90)	Bu_4NHF_2 (0.077)	CH_3CN	25	0.5	3	33
1,4-benzoquinone (1.1)	1 (1.3)	NH_4HF_2 (1.3)	CH_3CN	25	0.5	10	42
1,4-benzoquinone (0.60)	1 (0.70)	KF (1.7) + AcOH (0.70)	CH_3CN	25	0.25	10	34
1,4-benzoquinone (1.5)	1 (1.8)	NaCN (0.31)	CH_3CN	25	42	3	41
1,4-benzoquinone (1.5)	1 (1.8)	KCN (4.5)	CH_3CN	25	1	3	64
1,4-benzoquinone (0.77)	1 (0.90)	NaOH (2.3)	CH_3CN	25	2	3	29
1,4-benzoquinone (0.77)	1 (0.90)	LiN_3 (2.3)	CH_3CN	25	22	3	43
1,4-benzoquinone (0.77)	1 (0.90)	$(Et_2N)_3P$ (?)	CH_3CN	25	24	3	63
1,4-benzoquinone (0.77)	1 (0.90)	$(EtO)_3P$ (0.15)	CH_3CN	25	21	3	51
1,4-benzoquinone (0.80)	1 (0.80)	DMAP[d] (0.040)	CH_3CN	25	on[b]	3	50
1,4-benzoquinone (0.080)	1 (0.080)	K_2CO_3 (0.16)	DMF	25	1	3	53
1,4-benzoquinone (0.80)	2 (0.80)	K_2CO_3 (0.16)	DMF	25	1	4	52
2,6-di-*tert*-butyl-1,4-benzoquinone (0.80)	1 (0.80)	K_2CO_3 (0.16)	CH_3CN	25	22	5	41
3,5-di-*tert*-butyl-1,2-benzoquinone (0.80)	1 (0.80)	K_2CO_3 (0.16)	CH_3CN	25	24	6	83
1,4-naphthoquinone (0.80)	1 (0.80)	K_2CO_3 (0.16)	DMF	25	2	7	41
9,10-anthraquinone (0.80)	1 (0.80)	K_2CO_3 (0.16)	DMF	25	5	8	82
9,10-phenanthrenequinone (0.80)	1 (0.80)	K_2CO_3 (0.16)	DMF	25	4	9	83

[a] Not optimized. [b] on = overnight. [c] nd = not determined. [d] DMAP = 4-(dimethylamino)pyridine.

2, and potassium fluoride. These are shown in Table I. In general these reactions were clean and gave high yields. The similar reactivity of silanes 1 and 2 suggests that the alkyl groups bound to silicon have little effect on this process.

The scope of the addition process relative to the structure of the starting quinone was studied in some detail. In general, unsubstituted or alkyl-substituted quinones participate in the reaction (Table I) but halogen-substituted quinones do not. For example, treatment of 2-chloro-1,4-benzoquinone with 1 and potassium fluoride in acetonitrile led to consumption of the quinone but formation of only a trace of two addition products (presumably 16 and 17). Similarly, 3,4,5,6-tetrachloro-1,2-benzoquinone and 2,3,5,6-tetrafluoro-1,4-benzoquinone did not react cleanly.

N,N-Dimethylformamide (DMF) was found to be a suitable replacement for acetonitrile as solvent when the solubility of the quinone in acetonitrile is low, as in the cases of anthraquinone and phenanthrenequinone. Other solvents may also be used, as 3 was synthesized in sulfolane. However, 3 was not detected in a mixture of 1,4-benzoquinone, 1, and potassium fluoride in toluene. Apparently a solvent must be chosen in which both the substrate and potassium fluoride have some solubility.

In the reactions described so far potassium fluoride was used in excess (2 or 3 equiv relative to the quinone). Under these conditions the reactions, in most cases, occurred within a few minutes of mixing the reagents at room temperature. Subsequent experiments showed that potassium fluoride need be present only in catalytic amounts. However, such reactions were considerably slower and produced increased amounts of coproducts relative to those utilizing excess potassium fluoride. Typical coproducts are compounds like 18.

The use of potassium fluoride as a catalyst for the addition reaction has other disadvantages. Aside from the negative effects found when catalytic amounts are used, potassium fluoride is fairly expensive and very difficult to dry. Dryness of the reaction mixtures is important as the silane 1 is rapidly converted to triethylsilanol in the presence of water and base. In addition, we have experienced difficulty in initiating reactions, particularly on a large scale. This is a typical problem associated with heterogeneous mixtures that is probably related to the nature of the solid surface. The addition reactions are exothermic and are typically conducted at large scale by slow addition of the silane (1 or 2) to a mixture of the other reactants. In some experiments late initiation resulted in an uncontrollable exotherm that afforded low yields of product. In other experiments the reaction did not initiate at all.

A variety of materials were tested for their ability to catalyze the addition of silanes 1 or 2 to quinones. The results, which are shown in Table II, show the wide range of compounds that catalyze the reaction. All the successful catalysts are basic, but the data do not suggest a correlation between base strength and catalytic activity. Some of the materials tested were active even though they are known to react independently with other components of the reaction mixture. For example, a large amount of triethylsilanol was observed along with the expected addition product when sodium hydroxide was used as catalyst. Reactions would not proceed to completion when triethyl phosphite was used as catalyst due to the consumption of the phosphite by unreacted quinone, a known process.[14]

The data in Table II suggest that potassium carbonate is a preferred catalyst. This material is both less expensive and less hygroscopic than potassium fluoride. In addition, a catalytic amount of potassium carbonate (20 mol %) in DMF afforded reaction rates and yields comparable to those obtained with excess potassium fluoride in acetonitrile (Table I).

It is noteworthy that treatment of 1,4-benzoquinone and silane 1 with ammonium bifluoride or a mixture of potassium fluoride and a proton source (acetic acid) as catalyst afforded the alcohol 10 directly. This alcohol may also be synthesized by desilylation of compound 3 (vide infra).

With a variety of dienones in hand, we examined reported reactions of similar compounds for methods by which various trifluoromethylated arenes might be produced. Simple acid-catalyzed hydrolyses were carried out, affording alcohols 10–15 in yields ranging from 73 to 98%.

Dissolving metal reduction of either silylated or desilylated dienones afforded, in most cases, the (trifluoromethyl)phenols. The unsubstituted dienones 3, 4, and 10 were easily reduced with zinc and acetic acid to give the known phenol 19.[11] When made from compound 3, phenol 19 could not be separated by preparative thin layer chromatography (PTLC) or distillation from triethylsilanol.

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However, alcohol **10** afforded **19**, which was easily purified by PTLC, and dienone **4** afforded a mixture of **19** and tri-*n*-butylsilanol, which was separated by distillation. Compounds **5**, **6**, and **7** remained essentially unchanged on treatment with zinc and acetic acid but were readily reduced to phenols **20**, **21**, and **22** with aluminum amalgam in wet THF. Compounds **8** and **9** did not afford phenols under similar conditions but underwent only partial reduction. Such increased resistance to aromatization with increasing substitution of the dienone has been reported in other systems.[15]

The conversion of a dienone into an aniline has been reported in the literature.[16] We found that treatment of **3** or **10** under the described conditions gave 4-(trifluoromethyl)aniline (**23**) in good yield. This method was used to demonstrate the feasibility of the transformation but other, less expensive, reagents would probably suffice.[17]

Experimental Section

General. NMR spectra were recorded on a Varian EM-390 or a GE/NIC NT-360 spectrometer. Proton chemical shifts are reported in parts per million relative to tetramethylsilane and fluorine chemical shifts are reported in parts per million relative to fluorotrichloromethane. Mass spectra were recorded on a Finnigan 4023 gas chromatograph/mass spectrometer equipped with a 50-m SE-52 fused silica capillary column. Gas chromatography was carried out on a Hewlett-Packard 5890 instrument equipped with a 30 m × 0.53 mm i.d. × 2.65 μm (film thickness) HP-5 fused silica capillary column. Preparative thin layer chromatography (PTLC) was carried out on commercially prepared silica gel plates (Analtech) and visualization was by ultraviolet light. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Triethyl(trifluoromethyl)silane (1). A flask equipped with a dry ice condenser was flame dried under a nitrogen stream and charged with 25 g (0.17 mol) of chlorotriethylsilane and 40 mL of dichloromethane. After cooling the resulting solution to −78 °C and charging the condenser with dry ice and acetone, 40 mL (0.43 mol) of bromotrifluoromethane (Freon 13B1) that had been condensed into a graduated tube was warmed to room temperature and allowed to distill into the flask. The cold solution was treated dropwise with 66 mL (0.24 mol) of hexaethylphosphorous triamide, allowed to stir at −78 °C for 2 h, and allowed to stir at room temperature overnight. Low boiling components were then short-path distilled into a cold (−78 °C) receiving flask at ≥1 Torr with the pot temperature kept at <50 °C. The distillate was further fractionated by removal of the dichloromethane (40–45 °C at atmospheric pressure) and short-path distillation to give 22.0 g of 98% pure (69% yield) triethyl(trifluoromethyl)silane (**1**): bp 52–54 °C at 10 Torr; ^{1}H NMR ($CDCl_3$) δ 0.59–1.16 (m); ^{19}F NMR ($CDCl_3$) −61.3 ppm (s); IR (neat) 2960, 2915, 2882, 1458, 1413, 1206, 1055, 1020, 734, 693 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 115 (66, M − CF_3), 105 (46), 87 (85), 77 (100), 59 (56), 49 (41), 47 (37), 41 (38). Anal. Calcd for $C_7H_{15}F_3Si$: C, 45.62; H, 8.20. Found: C, 45.59; H, 8.13.

Tri-*n*-butyl(trifluoromethyl)silane (2). A flask equipped with a dry ice condenser was flame dried under a nitrogen stream and charged with 5.0 g (21 mmol) of chlorotri-*n*-butylsilane and 10 mL of dichloromethane. After cooling the resulting solution to −78 °C and charging the condenser with dry ice and acetone, 6.2 mL (66 mmol) of bromotrifluoromethane (Freon 13B1) that had been condensed into a graduated tube was warmed to room temperature and allowed to distill into the flask. The cooling bath was removed and the mixture was allowed to warm to the temperature of the refluxing Freon (−59 °C). To this cold solution was added, dropwise, 8.0 mL (29 mmol) of hexaethylphosphorous triamide. The resulting solution was stirred at reflux for 1 h. Removal of the condenser and continued stirring for 1 h resulted in evaporation of excess Freon and warming of the solution to room temperature. Dilution with 30 mL of dichloromethane, water (three 30-mL portions), and 1 N HCl (two 30-mL portions) washing, drying ($MgSO_4$), and concentration afforded a residue that was short-path distilled to give 3.6 g (64% yield) of tri-*n*-butyl(trifluoromethyl)silane (**2**): bp 53–58 °C at 0.5 Torr; ^{1}H NMR ($CDCl_3$) δ 0.60–1.10 (m, 5 H), 1.10–1.56 (m, 4 H); ^{19}F NMR ($CDCl_3$) −61.6 ppm (s); IR (neat) 2956, 2925, 2872, 1214, 1058 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 199 (30, M − CF_3), 143 (80), 105 (30), 101 (27), 87 (30), 77 (66), 63 (43), 59 (41), 55 (54), 47 (25), 43 (20), 41 (100). Anal. Calcd for $C_{13}H_{27}F_3Si$: C, 58.16; h, 10.14. Found: C, 58.26; H, 10.09.

4-(Triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (3). A mixture of 195 mg (3.3 mmol) of potassium fluoride (Allied, dried at 200 °C, 25 Torr overnight), 179 mg (1.7 mmol) of 1,4-benzoquinone, and 2 mL of acetonitrile (dried over 3A molecular sieves) was treated with 456 mg (2.6 mmol) of triethyl(trifluoromethyl)silane (**1**) and stirred vigorously at room temperature for 1 h. The mixture was filtered and the filter cake washed with three 2-mL portions of dichloromethane. Concentration of the combined filtrates gave a black oil, which was dissolved in dichloromethane and loaded onto a column of 2 g of silica gel (230–400 mesh). The column was washed with dichloromethane until the eluent contained no UV-active material. Concentration of the eluent gave a black oil, which was purified by PTLC (one 2-mm silica gel plate eluted with 50% dichloromethane–50% petroleum ether) to give 348 mg (72% yield) of 4-(triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**3**) as an amber liquid: bp 68–78 °C (0.5 Torr); ^{1}H NMR ($CDCl_3$) δ 0.40–1.06 (m, 15 H), 6.41 (d, 2 H, *J* = 9 Hz), 6.89 (d, 2 H, *J* = 9 Hz); ^{19}F NMR ($CDCl_3$) −83.8 ppm (t, J_{FH} = 4 Hz); IR (neat) 2956, 2912, 2877, 1677, 1611, 1265, 1240, 1182, 1129, 1067, 1004, 835, 749, 732 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 263 (6, M − C_2H_5), 139 (79), 111 (100), 105 (68), 83 (41), 77 (100), 47 (31), 45 (35). Anal. Calcd for $C_{13}H_{19}F_3O_2Si$: C, 53.39; H, 6.54. Found: C, 53.60; H, 6.79.

The following compounds (**4–9**) were prepared by similar procedures.

4-(Tri-*n*-butylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (4): 59% yield of yellow liquid; ^{1}H NMR ($CDCl_3$) δ 0.50–0.61 (m, 6 H), 0.85 (t, 9 H, *J* = 5 Hz), 1.19–1.35 (m, 12 H), 6.39 (d, 2 H, *J* = 9 Hz), 6.82 (d, 2 H, *J* = 9 Hz); ^{19}F NMR ($CDCl_3$) −80.0 ppm (s). Anal. Calcd for $C_{19}H_{31}F_3O_2Si$: C, 60.60; H, 8.30. Found: C, 60.76; H, 8.43.

2,6-Di-*tert*-butyl-4-(triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (5): 70% yield of pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ 0.39–1.10 (m, 15 H), 1.22 (s, 18 H), 6.50 (s, 2 H); ^{19}F NMR ($CDCl_3$) −80.5 ppm (s). Anal. Calcd for $C_{21}H_{35}F_3O_2Si$: C, 62.34; H, 8.72. Found: C, 62.44; H, 8.75.

4,6-Di-*tert*-butyl-2-(triethylsiloxy)-2-(trifluoromethyl)-3,5-cyclohexadien-1-one (6): 90% yield of yellow liquid; ^{1}H NMR ($CDCl_3$) δ 0.35–1.10 (m, 15 H), 1.16 (s, 3 H), 1.23 (s, 3 H), 5.85 (d, 1 H, *J* = 2 Hz), 6.84 (d, 1 H, *J* = 2 Hz); ^{19}F NMR ($CDCl_3$) −80.0 ppm (s). Anal. Calcd for $C_{21}H_{35}F_3O_2Si$: C, 62.34; H, 8.72. Found: C, 62.46; H, 8.69.

1,4-Dihydro-1-oxo-4-(triethylsiloxy)-4-(trifluoromethyl)-naphthalene (7): 44% yield of brown liquid; ^{1}H NMR ($CDCl_3$) δ 0.30–1.00 (m, 15 H), 6.65 (d, 1 H, *J* = 10 Hz), 7.06 (d, 1 H, *J* = 10 Hz), 7.50–8.30 (m, 4 H); ^{19}F NMR ($CDCl_3$) −79.6 ppm (s). Anal. Calcd for $C_{17}H_{21}F_3O_2Si$: C, 59.62; H, 6.18. Found: C, 59.91; H, 6.33.

9,10-Dihydro-9-oxo-10-(triethylsiloxy)-10-(trifluoromethyl)anthracene (8): 86% yield of colorless liquid that crystallized on standing; ^{1}H NMR ($CDCl_3$) δ 0.19–0.90 (m, 15 H), 7.50–7.90 (m, 4 H), 7.90–8.13 (m, 2 H), 8.30–8.47 (m, 2 H); ^{19}F NMR ($CDCl_3$) −79.9 ppm (t, J_{FH} = 14 Hz). Anal. Calcd for $C_{21}H_{23}F_3O_2Si$: C, 64.26; H, 5.91. Found: C, 64.26; H, 6.01.

9,10-Dihydro-9-oxo-10-(triethylsiloxy)-10-(trifluoromethyl)phenanthrene (9): 86% yield of colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.45–1.17 (m, 15 H), 7.31–8.10 (m, 8 H); ^{19}F NMR ($CDCl_3$) −79.4 ppm (s). Anal. Calcd for $C_{21}H_{23}F_3O_2Si$: C, 64.26; H, 5.91. Found: C, 64.28; H, 5.92.

4-Hydroxy-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (10). A mixture of 200 mg (0.68 mmol) of 4-(triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**3**) and 1 mL of a solution of 1 part 37% hydrochloric acid in 9 parts absolute ethanol

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was heated at reflux overnight and poured into 10 mL of water. The resulting aqueous mixture was extracted with three 10-mL portions of dichloromethane. Combination, drying ($MgSO_4$), and concentration of the organic layers afforded a residue, which was purified by PTLC (one 2-mm silica gel plate eluted with 1% methanol–99% dichloromethane) to give 109 mg (89% yield) of 4-hydroxy-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**10**). An analytical sample was obtained by crystallization from dichloromethane–hexane: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 3.40 (br s, 1 H), 6.40 (d, 2 H, J = 10 Hz), 6.89 (d, 2 H, J = 10 Hz); ^{13}C NMR ($CDCl_3$) 70.2 (q, J_{CF} = 30 Hz), 125.0 (q, J_{CF} = 286 Hz), 132.3 (d), 142.7 (d), 184.5 (s) ppm; ^{19}F NMR ($CDCl_3$) –79.6 ppm (s); IR (KBr) 3374, 3105, 3022, 2919, 1693, 1671, 1632, 1620, 1396, 1249, 1235, 1195, 1174, 1089, 1078, 1003, 988, 980, 973, 863, 698 cm^{-1}; mass spectrum (70 eV) m/z (relative intensity) 178 (5, M^+), 109 (100), 81 (34); 53 (36). Anal. Calcd for $C_7H_5F_3O_2$: C, 47.20; H, 2.83. Found: C, 47.42; H, 2.80.

The following compounds (**11–15**) were prepared by similar procedures.

2,6-Di-*tert*-butyl-4-hydroxy-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (11): 98% yield; mp 93–94 °C; ^1H NMR ($CDCl_3$) δ 1.25 (s, 18 H), 2.57 (s, 1 H), 6.48 (s, 2 H); ^{19}F NMR ($CDCl_3$) –79.8 to –79.9 ppm (m). Anal. Calcd for $C_{15}H_{12}F_3O_2$: C, 62.05; H, 7.29. Found: C, 61.98; H, 7.46.

4,6-Di-*tert*-butyl-2-hydroxy-2-(trifluoromethyl)-3,5-cyclohexadien-1-one (12): 87% yield; mp 58–61 °C; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9 H), 1.25 (s, 9 H), 4.32 (s, 1 H), 5.96 (d, 1 H, J = 2 Hz), 6.93 (d, 1 H, J = 2 Hz); ^{19}F NMR ($CDCl_3$) –79.5 ppm (s). Anal. Calcd for $C_{15}H_{12}F_3O_2$: C, 62.05; H, 7.29. Found: C, 62.16; H, 7.27.

1,4-Dihydro-4-hydroxy-1-oxo-4-(trifluoromethyl)-naphthalene (13): 73% yield; mp 73–76 °C; ^1H NMR ($CDCl_3$) δ 3.94 (s, 1 H), 6.48 (d, 1 H, J = 10 Hz), 7.02 (d, 1 H, J = 10 Hz), 7.43–8.18 (m, 4 H); ^{19}F NMR ($CDCl_3$) –80.0 ppm (s). Anal. Calcd for $C_{11}H_7F_3O_2$: C, 57.90; H, 3.09. Found: C, 57.94; H, 3.12.

9,10-Dihydro-10-hydroxy-9-oxo-10-(trifluoromethyl)-anthracene (14): 90% yield; mp 153–155 °C; ^1H NMR ($CDCl_3$) δ 3.56 (s, 1 H), 7.47–7.82 (m, 4 H), 7.92–8.31 (m, 4 H); ^{19}F NMR ($CDCl_3$) –79.8 ppm (s). Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26. Found: C, 64.63; H, 3.29.

9,10-Dihydro-10-hydroxy-9-oxo-10-(trifluoromethyl)-phenanthrene (15): 96% yield; mp 148–151 °C; ^1H NMR ($CDCl_3$) δ 4.76 (s, 1 H), 7.22–8.07 (m, 8 H); ^{19}F NMR ($CDCl_3$) –78.5 ppm (s). Anal. Calcd for $C_{15}H_9F_3O_2$: C, 64.75; H, 3.26. Found: C, 64.75; H, 3.30.

4-(Trifluoromethyl)phenol (19). A solution of 3.9 g (10 mmol) of 4-(tri-*n*-butylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**4**) in 10 mL of absolute ethanol was treated successively with 1.3 g (20 mmol) of zinc dust and 10 mL of a solution of 80% acetic acid–20% water. The mixture was heated to reflux for 1 h, allowed to cool to room temperature, and poured into 100 mL of water. The resulting aqueous mixture was extracted with three 50-mL portions of diethyl ether. Combination, drying ($MgSO_4$), and concentration of the ether layers afforded a residue, which purified by short-path distillation to give 0.80 g (47% yield) of 4-(trifluoromethyl)phenol (**19**): bp 60–65 °C at 5 Torr (lit.[11] bp 71.5–72 °C at 8 Torr); mass spectrum (70 eV) m/z (relative intensity) 162 (100, M^+), 143 (56), 112 (31), 39 (22).

2,6-Di-*tert*-butyl-4-(trifluoromethyl)phenol (20). A strip of aluminum foil weighing 264 mg (9.8 mmol) was amalgamated by immersion in a solution of 2% mercuric chloride in water for 15 s, washed with absolute ethanol followed by diethyl ether, cut into small pieces, and added to a solution of 412 mg of 96% pure (0.98 mmol) 2,6-di-*tert*-butyl-4-(triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**5**) in 25 mL of 10% water–90% tetrahydrofuran. The resulting mixture was heated at 70 °C for 1.5 h, allowed to cool to room temperature, and filtered. The filter cake was washed with tetrahydrofuran. Concentration of the combined filtrates gave a residue, which was poured into 25 mL of water. The aqueous mixture was extracted with three 10-mL portions of dichloromethane. Combination, drying ($MgSO_4$), and concentration of the organic layers gave a residue, which was purified by PTLC (one 2-mm silica gel plate eluted with petroleum ether), affording 247 mg of 95% pure (87% yield) 2,6-di-*tert*-butyl-4-(trifluoromethyl)phenol (**20**). An analytical sample was obtained by crystallization from methanol: mp 78–80 °C; ^1H NMR ($CDCl_3$) δ 1.45 (s, 18 H), 5.56 (br s, 1 H), 7.50 (s, 1 H); ^{19}F NMR ($CDCl_3$) –61.7 ppm (s); IR (KBr) 3632, 2963, 1337, 1319, 1241, 1167, 1141, 1109, 893, 668 cm^{-1}; mass spectrum (70 eV) m/z (relative intensity) 274 (20, M^+), 259 (100), 231 (28), 57 (57), 41 (54). Anal. Calcd for $C_{15}H_{21}F_3O$: C, 65.67; H, 7.72. Found: C, 65.46; H, 7.94.

The following compounds (**21** and **22**) were prepared by similar procedures.

2,4-Di-*tert*-butyl-6-(trifluoromethyl)phenol (21): 83% yield of colorless liquid; ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H), 1.45 (s, 9 H), 5.56 (q, 1 H, J_{HF} = 4 Hz), 7.39 (d, 1 H, J = 2 Hz), 7.54 (d, 1 H, J = 2 Hz); ^{19}F NMR ($CDCl_3$) –59.8 ppm (d, J = 5 Hz). Anal. Calcd for $C_{15}H_{21}F_3O$: C, 65.67; H, 7.72. Found: C, 65.87; H, 7.94.

4-(Trifluoromethyl)-1-naphthol (22): 90% yield; mp 132–133 °C; ^1H NMR ($CDCl_3$) δ 5.50 (br s, 1 H), 6.79 (d, 1 H, J = 8 Hz), 7.50–7.80 (m, 3 H), 8.10–8.45 (m, 2 H); ^{19}F NMR ($CDCl_3$) –59.5 ppm (s). Anal. Calcd for $C_{11}H_7F_3O$: C, 62.27; H, 3.33. Found: C, 62.42; H, 3.50.

4-(Trifluoromethyl)aniline (23). A mixture of 400 mg (1.4 mmol) of 4-(triethylsiloxy)-4-(trifluoromethyl)-2,5-cyclohexadien-1-one (**3**), 572 mg (4.2 mmol) of ethyl glycinate hydrochloride, 298 mg (3.6 mmol) of sodium bicarbonate, and 10 mL of 95% ethanol was heated to reflux for 6 h, allowed to cool to room temperature, and poured into 25 mL of water. The resulting aqueous mixture was extracted with three 10-mL portions of dichloromethane. The organic layers were combined and extracted with six 5-mL portions of 1 N HCl. Combination of the aqueous layers and treatment with solid sodium bicarbonate until neutral to pH paper gave a cloudy mixture that was extracted with three 10-mL portions of dichloromethane. The organic layers were combined, dried ($MgSO_4$), and stripped to give a residue, which was purified by PTLC (one 2-mm silica gel plate eluted with dichloromethane), affording 160 mg (73% yield) of 4-(trifluoromethyl)aniline (**23**).[11]

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