

Supporting Information for
Reaction of Benzyne with Salicylaldehydes: General Synthesis of Xanthenes, Xanthones, and Xanthols

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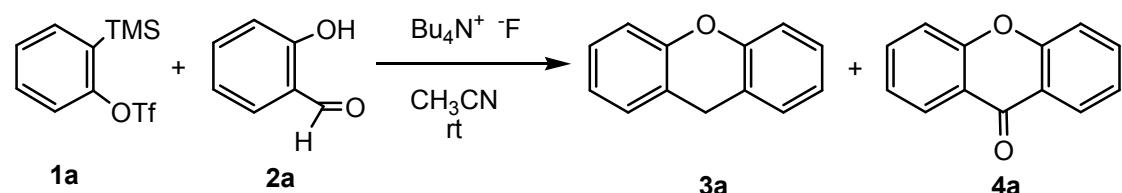
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Materials: All reagents were purchased from TCI or Aldrich. Authentic samples were purchased from Aldrich.

Reaction of Benzenediazonium Carboxylate with Salicylaldehyde 2a

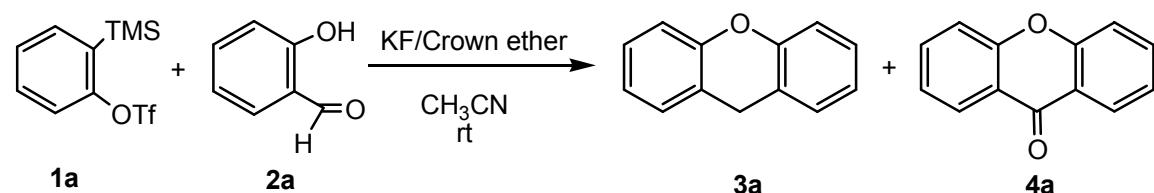
To a refluxing solution of salicylaldehyde **2a** (62 mg, 0.5 mmol) in tetrahydrofuran (5 mL) was added benzenediazonium carboxylate (370 mg, 2.5 mmol) in portionwise. After refluxing for 4h, the reaction mixture was evaporated to give a brown oil. The ¹H NMR of the reaction mixture showed unidentified complex peaks.

Reaction of Triflate 1a with Salicylaldehyde 2a followed by the Addition of Tetrabutylammonium Fluoride



To a solution of triflate **1a** (180 mg, 0.60 mmol) and salicylaldehyde **2a** (62 mg, 0.50 mmol) in acetonitrile (5 mL) was added tetrabutylammonium fluoride (0.10 mol/L, 5.5 mL, 0.55 mmol) dropwise for 2 h. After stirring for 13 h, saturated sodium chloride solution was added to the reaction mixture, and extracted with dichloromethane (7 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with hexane-ethyl acetate (10:1) to give xanthene **3a** (9 mg, 0.05 mmol) and xanthone **4a** (11 mg, 0.06 mmol). Xanthene **3a**: mp 99-100 °C. Its mp was identical with the authentic sample (mp 100-101 °C). ¹H NMR (CDCl₃) δ = 4.01 (s, 2H, CH₂), 6.95-7.20 (m, 8H, Ar). ¹³C NMR (CDCl₃) δ = 27.93, 116.57, 120.57, 122.89, 127.60, 128.83, 151.98. Xanthone **4a**: mp 172-173 °C. Its mp was identical with the authentic sample (mp 174-176 °C). ¹H NMR (CDCl₃) δ = 7.32 (dd, 1H, J = 7.6 and 8.0 Hz, Ar), 7.41 (d, 1H, J = 7.6 Hz, Ar), 7.67 (dd, 1H, J = 7.6 and 8.0 Hz, Ar), 8.27 (d, 1H, J = 7.6 Hz, Ar). ¹³C NMR (CDCl₃) δ = 117.83, 121.90, 123.67, 126.86, 134.67, 156.01, 177.00.

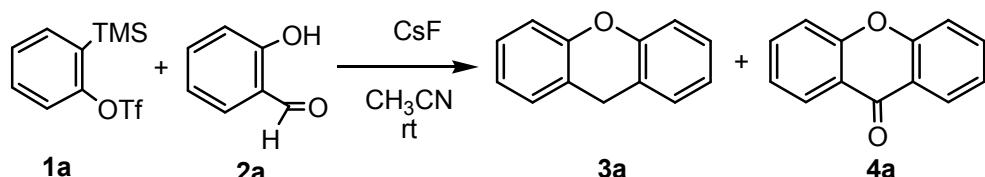
Reaction of Triflate 1a with Salicylaldehyde 2a followed by the Addition of Potassium Fluoride



To a solution of triflate **1a** (181 mg, 0.60 mmol), salicylaldehyde **2a** (62 mg, 0.50 mmol), 18-crown-6 (264 mg, 1.0 mmol) in acetonitrile (5 mL) was added potassium fluoride (0.121 g, 2.01 mmol) in one portion. After stirring for 19 h, saturated sodium chloride solution was added to the reaction mixture, and extracted with ether (7 mL x 3). The combined extracts

were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with hexane-ethyl acetate (10:1) to give xanthene **3a** (37 mg, 0.20 mmol) and xanthone **4a** (46 mg, 0.23 mmol).

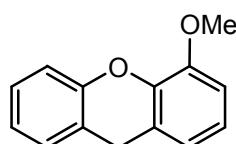
Reaction of Triflate **1a with Salicylaldehyde and CsF.**



To a solution of triflate **1a** (360 mg, 1.2 mmol) and salicylaldehyde **2a** (120 mg, 1.0 mmol) in acetonitrile (5 mL) was added CsF (460 mg, 3.0 mmol) in one portion. After stirring for 15h, the reaction mixture was poured into aq. Na₂CO₃ (10%). The resulting mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with ethyl acetate-hexane (1:10) to afford xanthene **3a** (82 mg, 0.42 mmol) and xanthone **4a** (88 mg, 0.46 mmol).

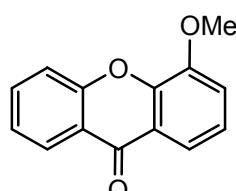
Reaction of Triflate **1a with 2-Hydroxy-3-methoxybenzaldehyde and CsF.**

To a solution of triflate **1a** (330 mg, 1.1 mmol) and 2-hydroxy-3-methoxybenzaldehyde **2b** (152 mg, 1.0 mmol) in acetonitrile (5 mL) was added CsF (460 mg, 3.0 mmol) in one portion. After stirring for 15h, the reaction mixture was poured into aq. Na₂CO₃ (10%). The resulting mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with ethyl acetate-hexane (1:10) to afford 4-methoxy-9*H*-xanthene **3b** (89 mg, 0.42 mmol) and 4-methoxyl-9*H*-xanthone **4b** (106 mg, 0.47 mmol).



3b 4-Methoxy-9*H*-xanthene (**3b**): colorless oil (lit.¹ 120-130 °C/0.2 mmHg)

¹H NMR (CDCl₃) δ= 3.93 (s, 3H, CH₃), 4.05 (s, 2H, CH₂), 6.76-6.82 (m, 2H, Ar), 6.97 (dd, 1H, J=7.6 and 8.0Hz, Ar), 7.04 (δ, 1H, J= 8.0 Hz, Ar), 7.15-7.19 (m, 3H, Ar). ¹³C NMR (CDCl₃) δ=27.89, 56.14, 110.11, 116.81, 120.39, 120.64, 121.52, 122.58, 123.12, 127.60, 128.78, 141.51, 148.02, 151.73.

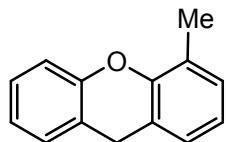


4-Methoxy-9*H*-xanthone (**4b**): colorless crystals, mp 174-175 °C (lit.² 173-174 °C)

¹H NMR (CDCl₃) δ = 4.05 (s, 3H, OCH₃), 7.26 (d, 1H, Ar), 7.32 (dd, 1H, *J*= 7.6 and 8.0 Hz, Ar), 7.40 (dd, 1H, *J*= 7.6 and 8.0 Hz, Ar), 7.63 (d, 1H, *J*= 7.6 Hz, Ar), 7.74 (dd, 1H, *J*= 7.6 and 8.0 Hz, Ar), 7.92 (d, 1H, *J*= 7.6 Hz, Ar), 8.35 (d, 1H, *J*= 8.0 Hz, Ar). ¹³C NMR (CDCl₃) δ = 56.65 (OMe), 115.56, 117.83, 118.51, 121.90, 122.93, 123.67, 124.31, 126.86, 135.01, 146.75, 148.85, 156.17, 177.40. MS: Found: 226.06. Calcd for C₁₄H₁₀O₃; M⁺: 226.03.

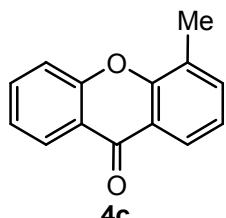
Reaction of Triflate **1a** with 2-Hydroxy-3-methylbenzaldehyde and CsF.

To a solution of triflate **1a** (330 mg, 1.1 mmol) and 2-hydroxy-3-methylbenzaldehyde **2c** (136 mg, 1.0 mmol) in acetonitrile (5 mL) was added CsF (460 mg, 3.0 mmol) in one portion. After stirring for 15h, the reaction mixture was poured into aq. Na₂CO₃ (10%). The resulting mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with ethyl acetate-hexane (1:10) to afford 4-methyl-9*H*-xanthene **3c** (84 mg, 0.43 mmol) and 4-methyl-9*H*-xanthone **4c** (97 mg, 0.46 mmol).



3c 4-Methyl-9*H*-xanthene (**3c**): colorless crystals mp 38-40 °C (lit.¹ mp 40°C).

¹H NMR (CDCl₃) δ=2.36 (s, 3H, CH₃), 4.02 (s, 2H, CH₂), 6.92 (dd, 1H, *J*= 7.6 Hz, 9.8 Hz, Ar), 6.95 -7.22 (m, 6H, Ar).

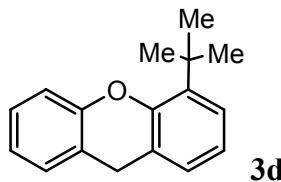


4c 4-Methyl-9*H*-xanthone (**4c**): colorless crystals: mp 125-126 °C. (lit.³ 126 °C).

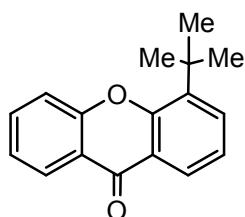
¹H NMR (CDCl₃) δ = 2.54 (s, 3H, CH₃), 7.25 (dd, 1H, *J*= 7.6 Hz, 7.0 Hz, Ar), 7.36 (dd, *J*= 7.6 Hz, 7.0 Hz, Ar), 7.50 (d, 1H, *J*= 7.6 Hz □ Ar), 7.53 (d, 1H, *J*= 7.2 Hz, Ar), 7.70 (dd, 1H, *J*= 7.2 Hz, Ar), 8.17 (d, 1H, *J*= 7.6 Hz, Ar), 8.32 (d, 1H, *J*= 8.0 Hz, Ar). ¹³C NMR (CDCl₃) δ = 16.04 (Me), 118.26 (CH), 121.84, 121.85, 123.62 (CH), 124.07 (CH), 124.51 (CH), 126.88 (CH), 127.47 (Ar), 134.88 (CH), 135.92 (CH), 154.74 (Ar), 156.26 (Ar), 177.76 (C=O).

Reaction of Triflate **1a** with 2-Hydroxy-3-*tert*-butylbenzaldehyde and CsF.

To a solution of triflate **1a** (330 mg, 1.1 mmol) and 2-hydroxy-3-*tert*-butylbenzaldehyde **2d** (178 mg, 1.0 mmol) in acetonitrile (5 mL) was added CsF (460 mg, 3.0 mmol) in one portion. After stirring for 15h, the reaction mixture was poured into aq. Na₂CO₃ (10%). The resulting mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with ethyl acetate-hexane (1:10) to afford 4-*tert*-butyl-9*H*-xanthene **3d** (50 mg, 0.21 mmol) and 4-*tert*-butyl-9*H*-xanthone **4d** (66 mg, 0.26 mmol).



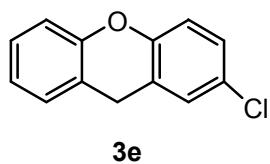
4-*tert*-Butyl-9*H*-xanthene (3d): colorless oil. ^1H NMR (CDCl_3) δ = 1.48 (s, 9H, CH_3), 4.00 (s, 2H, CH_2), 6.96 (dd, 1H, J = 7.2 and 7.6 Hz, Ar), 7.03-7.05 (m, 2H, Ar), 7.12 (d, 1H, J = 8.0 Hz, Ar), 7.16-7.20 (m, 3H, Ar). ^{13}C NMR (CDCl_3) δ = 29.01 (CH_2), 30.29 (Me), 35.08, 116.42, 122.04, 122.07, 122.70, 123.26, 125.15, 127.05, 127.68, 128.68, 137.77, 151.46, 152.47. HRMS: Found: 238.1363. Calcd M^+ : 238.1358.



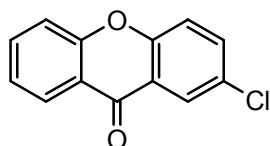
4-*tert*-Butyl-9*H*-xanthone (4d): colorless crystals; mp 129-131 °C. ^1H NMR (CDCl_3) δ = 1.58 (s, 9H, CH_3), 7.32 (dd, 1H, J = 7.6 and 8.0 Hz, Ar), 7.40 (dd, 1H, J = 7.6 and 8.0 Hz, Ar), 7.56 (d, 1H, J = 8.4 Hz, Ar), 7.71-7.75 (m, 2H, Ar), 8.26 (d, 1H, J = 8.0 Hz, Ar), 8.35 (d, 1H, J = 8.0 Hz, Ar). ^{13}C NMR (CDCl_3) δ = 30.10 (Me), 35.19, 117.87, 121.42, 122.49, 123.48, 123.93, 124.93, 126.67, 132.00, 134.73, 138.75, 154.96, 155.59, 177.70. HRMS: Found: 252.1150. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: M^+ 252.1151.

Reaction of Triflate **1a** with 2-Hydroxy-5-chlorobenzaldehyde and CsF.

To a solution of triflate **1a** (330 mg, 1.1 mmol) and 2-hydroxy-5-chlorobenzaldehyde **2e** (156 mg, 1.0 mmol) in acetonitrile (5 mL) was added CsF (460 mg, 3.0 mmol) in one portion. After stirring for 15h, the reaction mixture was poured into aq. Na_2CO_3 (10%). The resulting mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a brown oil, which was chromatographed over silica gel by elution with ethyl acetate-hexane (1:10) to afford 2-chloro-9*H*-xanthene **3e** (87 mg, 0.40 mmol) and 2-chloro-9*H*-xanthone **4e** (97 mg, 0.42 mmol).



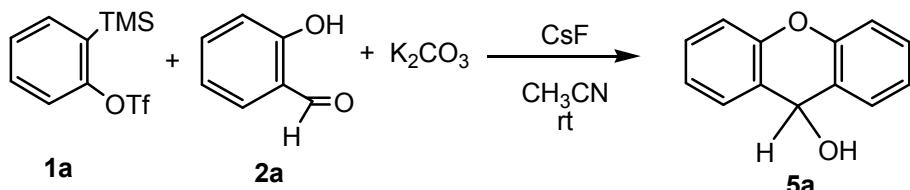
2-Chloro-9*H*-xanthene (3e): colorless crystals mp 114-115 °C. (lit.¹ mp 109-110 °C) ^1H NMR (CDCl_3) δ = 4.02 (s, 2H, CH_2), 6.97 (d, 1H, J = 8.0 Hz, Ar), 7.01-7.05 (m, 2H, Ar), 7.14-7.22 (m, 4H, Ar). ^{13}C NMR (CDCl_3) δ = 27.98 (CH_2), 116.72, 118.01, 119.89, 122.42, 123.49, 127.84, 127.87, 128.10, 128.77, 129.10, 150.77, 151.85. MS (EI): Found: 215.9. Calcd for $\text{C}_{13}\text{H}_9\text{ClO}$: M^+ 216.0.



4e

2-Chloro-9H-xanthone (**4e**): colorless crystals; mp 174-175 °C. (lit.⁴ mp 169-171 °C). ¹H NMR (CDCl₃) δ = 7.41 (dd, 1H, *J*= 7.2 and 7.6 Hz, Ar), 7.46-7.52 (m, 2H, Ar), 7.68 (d, 1H, *J*=8.0 Hz, Ar), 7.76 (dd, 1H, *J*= 7.6 and 8.0 Hz, Ar), 8.30-8.35 (m, 2H, Ar). ¹³C NMR (CDCl₃) δ = 118.05, 119.76, 121.49, 122.71, 124.29, 126.29, 126.82, 129.82, 129.73, 134.94, 135.20, 154.52, 156.08, 176.16. MS (EI) Found: 229.9. Calcd for C₁₃H₉ClO: M⁺ 230.0.

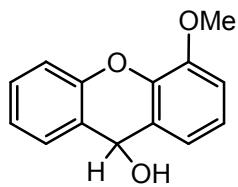
Reaction of Triflate **1a with Salicylaldehyde **2a** in the Presence of CsF and K₂CO₃.**



To a suspension of triflate **1a** (447 mg, 1.5mmol), salicylaldehyde **2a** (122 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 15 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 9-hydroxyxanthene (**5a**) (180 mg, 0.91 mmol). Colorless crystals: mp 127-128 °C. ¹H NMR spectral data and mp were identical with the authentic sample (mp 127-128 °C). ¹H NMR (CDCl₃) δ = 2.00 (d, *J*= 8.4 Hz, OH), 5.85 (d, 1H, *J*=8.4 Hz, CH), 7.08-7.24 (m, 4H, Ar), 7.36 (dd, 2H, *J*=6.8 and 7.6 Hz, Ar), 7.61 (d, 2H, *J*=7.6 Hz, Ar). MS: Found: 198.06. Calcd for C₁₃H₁₀O₂: M⁺ 198.02.

Reaction of Triflate **1a with 2-Hydroxyl-3-methoxylbenzaldehyde **2b** in the Presence of CsF and K₂CO₃.**

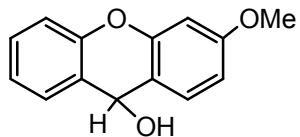
To a suspension of triflate **1a** (447 mg, 1.5mmol), benzaldehyde **2b** (152 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 15 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 4-methoxy-9-hydroxy-9H-xanthene (**5b**) (208 mg, 0.91 mmol).



5b: colorless crystals. mp 124-125 °C (lit.⁵ 125-128 °C). ¹H NMR (CDCl₃) δ = 2.48 (d, 1H, *J*=8.8 Hz, OH), 3.96 (s, 3H, OCH₃) 5.77 (d, 1H, *J*= 8.8 Hz, CH), 6.86 (d, 1H, *J*=8.0 Hz, Ar), 7.09 (dd, 1H, *J*=7.6 and 8.0 Hz, Ar), 7.07-7.16 (m, 2H, Ar), 7.20 (d, 1H, *J*=8.4 Hz, Ar), 7.28 (dd, 1H, *J*=6.8 and 8.0 Hz, Ar), 7.56 (d, 1H, *J*=7.6 Hz, Ar). ¹³C NMR (CDCl₃) δ = 56.33, 63.74, 111.40, 117.16, 121.31, 122.64, 123.22, 123.67, 123.76, 129.71, 129.85, 140.65, 147.84, 150.62.

Reaction of Triflate 1a with 2-Hydroxy-4-methoxylbenzaldehyde 2b' in the Presence of CsF and K₂CO₃.

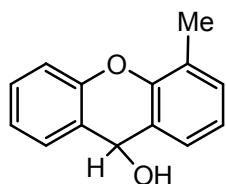
To a suspension of triflate **1a** (447 mg, 1.5mmol), salicylaldehyde **2b'** (152 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 15 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 3-methoxy-9-hydroxy-9H-xanthene (**5b'**) (194 mg, 0.85 mmol).



3-Methoxy-9-hydroxyxanthene (**5b'**): colorless crystals; mp 52-54 °C (lit.⁶ 52-53 °C). ¹H NMR (CDCl₃) δ = 1.96 (d, OH), 3.83 (s, 3H, OCH₃), 5.79 (d, 1H, CH), 6.68 (s, 1H, Ar), 6.76 (d, 1H, *J* = 7.6 Hz, Ar), 7.12-7.19 (m, 2H, Ar), 7.34(dd, 1H, *J* = 7.6 and 8.0 Hz, Ar), 7.49 (d, 1H, *J* = 7.6 Hz, Ar), 7.59 (d, 1H, *J* = 7.6 Hz, Ar). ¹³C NMR (CDCl₃) δ = 55.72 (OMe), 63.67, 101.06, 111.19, 115.32, 116.84, 123.13, 123.69, 129.74, 130.03, 130.77, 150.90, 151.88, 160.91.

Reaction of Triflate 1a with 2-Hydroxy-3-methylbenzaldehyde 2c in the Presence of CsF and K₂CO₃.

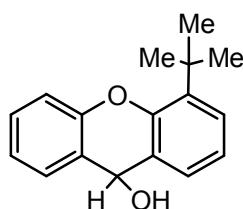
To a suspension of triflate **1a** (447 mg, 1.5mmol), salicylaldehyde **2c** (136 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 15 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 4-methyl-9-hydroxy-9H-xanthene (**5c**) (183 mg, 0.86 mmol).



4-Methyl-9-hydroxy-9H-xanthene (**5c**): colorless crystals; mp 88-90 °C. (lit.⁵ 89-92 °C). ¹H NMR (CDCl₃) δ = 1.84 (d, 1H, *J*=8.4 Hz, OH), 2.42 (s, 3H, CH₃), 5.83 (d, 1H, *J*=8.4 Hz, CH). MS: Found: 212.08. Calcd for C₁₀H₁₂O₂: M⁺: 212.23.

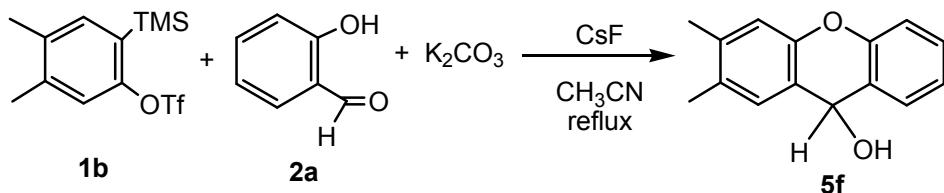
Reaction of Triflate **1a** with 2-Hydroxy-3-tert-butylbenzaldehyde **2d** in the Presence of CsF and K₂CO₃.

To a suspension of triflate **1a** (447 mg, 1.5 mmol), salicylaldehyde **2d** (178 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 15 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 4-*tert*-butyl-9-hydroxy-9H-xanthene (**5d**) (132 mg, 0.52 mmol).



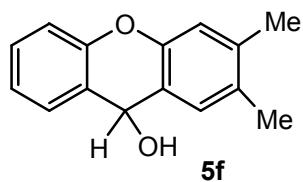
4-*tert*-Butyl-9-hydroxy-9H-xanthene (**5d**): colorless crystals; mp 129-131 °C. ¹H NMR (CDCl₃) δ = 1.50 (s, 9H, CH₃), 2.01 (d, 1H, *J*=8.4 Hz, OH), 5.83 (d, 1H, *J*=8.4 Hz, CH), 7.12 (dd, 1H, *J*= 6.4 and 7.2 Hz, Ar), 7.19 (dd, 1H, *J*=6.8 and 7.6 Hz, Ar), 7.25 (d, 1H, *J*=7.2 Hz, Ar), 7.35-7.37 (m, 2H, Ar), 7.47 (d, 1H, *J*=7.6 Hz, Ar), 7.60 (d, 1H, *J*=7.6 Hz, Ar). ¹³C NMR (CDCl₃) δ = 30.27 (Me), 35.29, 64.70, 116.81, 123.03, 123.17, 123.52, 123.69, 127.09, 127.82, 129.57, 129.75, 137.86, 149.91, 150.88. HRMS: Found: 254.1211. Calcd for C₁₃H₁₈O₂: M⁺ 254.1207.

Reaction of Triflate **1b** with Salicylaldehyde **2a** in the Presence of CsF and K₂CO₃.



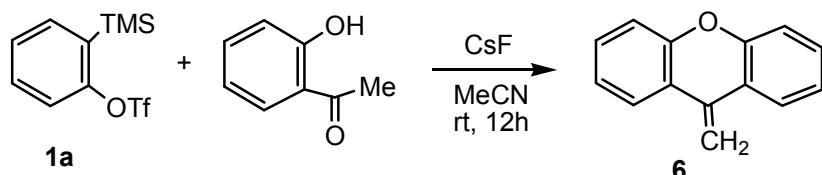
To a refluxing suspension of triflate **1b** (196 mg, 0.60 mmol), salicylaldehyde **2a** (61 mg, 0.5 mmol), and K₂CO₃ (148 mg, 1 mmol) in acetonitrile (5 mL) was added CsF (312 mg, 2.0 mmol) in one portion. After refluxing for 6 h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (7 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give pale yellow oily crystals,

which were chromatographed over alumina by elution with hexane-ethyl acetate (5:1) to afford 9-hydroxy-2,3-dimethyl-9*H*-xanthene (**5f**) (94 mg, 0.41 mmol).



9-Hydroxy-2,3-dimethyl-9*H*-xanthene **5f**: colorless crystals; mp 204-207 °C (lit.⁷ 208 °C). ¹H NMR (CDCl₃) δ = 2.18 (d, 1H, *J*= 6.8 Hz, OH), 2.26 (s, 3H, Me), 2.27 (s, 3H, Me), 5.79 (d, 1H, *J*=6.8 Hz, CH), 6.97 (s, 1H, Ar), 7.13-7.20 (m, 2H, Ar), 7.34 (s, 1H, Ar), 7.35 (dd, 1H, *J*= 7.6 and 8.0 Hz, Ar), 7.59 (d, 1H, *J* = 7.6 Hz). MS: Found: 226.09. Calcd for C₁₅H₁₄O₂: M⁺: 226.10.

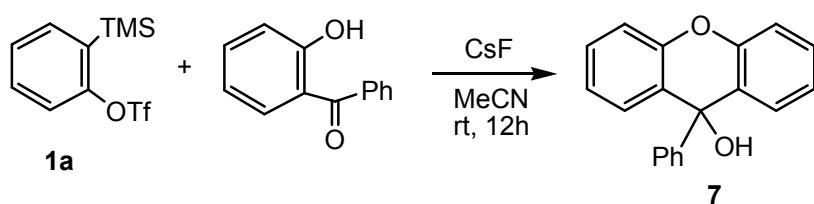
Reaction of Triflate **1a** with 2-Hydroxyacetophenone in the Presence of CsF



To a solution of triflate **1a** (447 mg, 1.5 mmol), 2-hydroxyacetophenone (136 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3.0 mmol) in acetonitrile (5 mL) was added CsF (456 mg, 3.0 mmol) in one portion. After stirring for 12h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane-ethyl acetate (5:1) to afford 9-methylenexanthene (**6**) (166 mg, 0.86mmol). colorless crystals: mp 110-111 °C (lit.⁸ 112 °C).

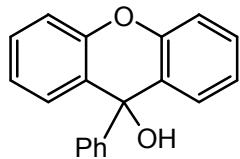
9-Methylenexanthene **6**: ¹H NMR (CDCl₃) δ = 5.51 (s, 2H, CH₂), 7.10-7.13 (m, 4H, Ar), 7.30 (dd, 2H, *J*=7.6 and 8.0 Hz, Ar), 7.73 (d, 2H, *J* = 8.0 Hz, Ar). ¹³C NMR (CDCl₃) δ = 77.45, 101.28, 117.47, 121.46, 123.56, 124.06, 129.74, 150.81. MS: Found: 194.01. Calcd for C₁₀H₁₀O: M⁺: 194.07.

Reaction of Triflate **1a** with 2-Hydroxybenzophenone in the Presence of CsF



To a solution of triflate **1a** (447 mg, 1.5 mmol), 2-hydroxyacetophenone (198 mg, 1.0 mmol), and K₂CO₃ (414 mg, 3.0 mmol) in acetonitrile (5 mL) was added CsF (456 g, 3.0 mmol) in one portion. After stirring for 12h, saturated NaCl (10 mL) was added to the reaction mixture and the mixture was extracted with ether (5 mL x 3). The combined extracts were dried over

sodium sulfate, filtered, and evaporated to give pale yellow oily crystals, which were chromatographed over alumina by elution with hexane-ethyl acetate (10:1) to afford 9-phenyl-9-hydroxyxanthene (**7**) (225 mg, 0.82 mmol). Colorless crystals mp 159-160 °C. ¹H NMR spectral data and mp were identical with the authentic sample (mp 160-161 °C).



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¹H NMR (CDCl₃) δ = 2.64 (s, OH), 7.05 (dd, 2H, *J* = 7.2 and 7.6 Hz, Ar), 7.24 (d, 2H, *J* = 7.2 Hz, Ar), 7.28-7.45 (m, 9H, Ar). ¹³C NMR (CDCl₃) δ = 70.66, 116.64, 123.80, 126.45, 126.98, 127.39, 128.20, 129.25, 129.32, 148.17, 149.89.

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