

One-Pot Synthesis of Xanthenes and Thioxanthenes by the Tandem Coupling-Cyclization of Arynes and Salicylates

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General procedures. All ^1H and ^{13}C spectra were recorded at 300 MHz and 75.5 MHz respectively. Thin layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) or a basic KMnO_4 solution. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI and 70 eV.

Reagents. All reagents were used directly as obtained commercially unless otherwise noted. Anhydrous forms of diethyl ether, ethyl acetate, and hexanes were purchased from Lancaster Synthesis, Inc. MeCN was dried by CaH, and THF solvent was dried over Na/benzophenone. Salicylates **1-6**, thiosalicylate **7**, aryne precursor **8** and CsF were purchased from Aldrich Chemical Co., Inc. Aryne precursors **9-11** were prepared according to literature procedures.¹

Representative procedure for the coupling-cyclization of arynes and salicylates. CsF (1.0 mmol), the salicylate (0.25 mmol), and the silylaryl triflate (0.28 mmol) in 5 mL of anhydrous THF were stirred at 65 or 90 °C for 24 h. The reaction mixture was allowed to cool to room temperature, diluted with diethyl ether (25 mL) and washed with brine (25 mL). The aqueous layer was re-extracted with diethyl ether (2 x 25 mL). The organic layers were

combined, dried (MgSO₄), filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel.

Representative procedure for the coupling-cyclization of arynes and thiosalicylates.

CsF (1.0 mmol) and the silylaryl triflate (0.28 mmol) were added to 5 mL of anhydrous THF, and the reaction vial was flushed with Ar. The thiosalicylate (0.25 mmol) was added in another 5 mL of anhydrous THF, and the mixture obtained was transferred to a reaction vial under Ar. The whole reaction solution was stirred at 65 or 90 °C for 24 h.

9H-Xanthen-9-one (12).² ¹H NMR (CDCl₃) δ 7.37 (t, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.70-7.74 (m, 2H), 8.33 (dd, *J* = 6.0, 1.2 Hz, 2H); ¹³C NMR (CDCl₃) 118.19, 122.06, 124.11, 126.93, 135.02, 156.37, 177.40; IR (CDCl₃) 2914, 2874, 1654, 1456 cm⁻¹; HRMS *m/z* 196.0527 (calcd for C₁₃H₈O₂, 196.0524).

2-Methoxy-9H-xanthen-9-one (13).³ ¹H NMR (CDCl₃) δ 3.91 (s, 3H), 7.26-7.49 (m, 4H), 7.69-7.72 (m, 2H), 8.33 (dd, *J* = 5.9, 0.8 Hz, 1H); ¹³C NMR (CDCl₃) 56.17, 105.96, 118.18, 119.64, 121.43, 122.29, 123.93, 125.14, 126.88, 134.80, 151.18, 156.15, 156.29, 177.29; IR (CDCl₃) 3014, 2981, 1666, 1467 cm⁻¹; HRMS *m/z* 226.0634 (calcd for C₁₄H₁₀O₃, 226.0630).

2-Acetyl-9H-xanthen-9-one (14).⁴ ¹H NMR (CDCl₃) δ 2.71 (s, 3H), 7.42 (td, *J* = 5.3, 0.7 Hz, 1H), 7.51-7.56 (m, 2H), 7.76 (td, *J* = 6.2, 1.3 Hz, 1H), 8.33-8.36 (m, 2H), 8.86 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (CDCl₃) 26.92, 118.37, 119.05, 121.36, 121.91, 124.90, 127.05, 128.56, 133.07, 134.07, 135.60, 156.17, 159.05, 176.90, 196.64; IR (CDCl₃) 3066, 2972, 1665, 1652 cm⁻¹; HRMS *m/z* 238.0632 (calcd for C₁₅H₁₀O₃, 238.0630).

2-Fluoro-9H-xanthen-9-one (15).⁵ ¹H NMR (CDCl₃) δ 7.35-7.51 (m, 4H), 7.73 (td, *J* = 7.2, 1.7 Hz, 1H), 7.95 (dd, *J* = 8.2, 2.8 Hz, 1H), 8.30 (dd, *J* = 7.9, 1.7 Hz, 1H); ¹³C NMR (CDCl₃) 111.59 (d, *J* = 13.7 Hz), 118.19, 120.20 (d, *J* = 8.1 Hz), 121.18, 122.82 (d, *J* = 7.0 Hz), 123.13 (d, *J* =

25.3 Hz), 124.34, 126.86, 135.29, 152.53 (d, $J = 1.6$ Hz), 156.29, 158.90 (d, $J = 245.5$ Hz), 176.68 (d, $J = 2.4$ Hz); IR (CDCl₃) 3087, 1664, 1157 cm⁻¹; HRMS m/z 214.0433 (calcd for C₁₃H₇FO₂, 214.0430).

7H-Benzo[c]xanthen-7-one (16).⁶ ¹H NMR (CDCl₃) δ 7.43 (t, $J = 7.7$ Hz, 1H), 7.64-7.77 (m, 5H), 7.88-7.92 (m, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 8.39 (dd, $J = 6.8, 1.5$ Hz, 1H), 8.63 (m, 1H); ¹³C NMR (CDCl₃) 117.81, 118.28, 121.69, 122.65, 123.10, 124.23, 124.28, 124.63, 126.78, 127.10, 128.30, 129.77, 134.56, 136.74, 153.84, 155.96, 177.09; IR (CDCl₃) 3061, 1654, 1439 cm⁻¹; HRMS m/z 246.0684 (calcd for C₁₆H₁₀O₂, 246.0681).

1-Methoxy-9H-xanthen-9-one (17).⁷ ¹H NMR (CDCl₃) δ 4.00 (s, 3H), 6.77 (d, $J = 8.1$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 1H), 7.26-7.40 (m, 2H), 7.55-7.67 (m, 2H), 8.29 (dd, $J = 8.0, 1.2$ Hz, 1H); ¹³C NMR (CDCl₃) 56.66, 105.60, 110.23, 112.79, 117.45, 123.24, 124.03, 127.02, 134.39, 135.04, 155.23, 158.35, 160.97, 176.74; IR (CDCl₃) 2971, 2946, 1666, 1474 cm⁻¹; HRMS m/z 226.0633 (calcd for C₁₄H₁₀O₃, 226.0630).

2,3-Dimethoxy-9H-xanthen-9-one (18).⁸ ¹H NMR (CDCl₃) δ 3.99 (m, 6H), 6.88 (t, $J = 3.7$ Hz, 1H), 7.33-7.45 (m, 2H), 7.63-7.69 (m, 2H), 8.32 (m, 1H); ¹³C NMR (CDCl₃) 56.58, 56.72, 99.82, 105.52, 115.07, 117.88, 121.68, 123.97, 126.72, 134.18, 146.88, 152.61, 155.60, 156.23, 176.27; IR (CDCl₃) 2940, 2834, 1648, 1466 cm⁻¹; HRMS m/z 256.0740 (calcd for C₁₅H₁₂O₄, 256.0736).

2,3-Dimethyl-9H-xanthen-9-one (19). ¹H NMR (CDCl₃) δ 2.35 (s, 3H), 2.38 (s, 3H), 7.23-7.45 (m, 3H), 7.68 (m, 1H), 8.04 (s, 1H), 8.32 (dd, $J = 7.9, 1.5$ Hz, 1H); ¹³C NMR (CDCl₃) 19.43, 20.80, 118.11, 118.34, 119.88, 122.13, 123.77, 126.50, 126.87, 133.26, 134.59, 145.68, 154.88, 156.35, 177.27; IR (CDCl₃) 2971, 2921, 1656, 1462 cm⁻¹; HRMS m/z 224.0840 (calcd for C₁₅H₁₂O₂, 224.0837).

9H-Thioxanthen-9-one (20).⁹ ¹H NMR (CDCl₃) δ 7.48 (td, *J* = 6.7, 1.5 Hz, 2H), 7.56-7.65 (m, 4H), 8.62 (dd, *J* = 7.4, 0.8 Hz, 2H); ¹³C NMR (CDCl₃) 126.21, 126.52, 129.47, 130.09, 132.49, 137.50, 180.18; IR (CDCl₃) 2971, 2919, 1684, 1459 cm⁻¹; HRMS *m/z* 212.0299 (calcd for C₁₃H₈OS, 212.0296).

1-Methoxy-9H-thioxanthen-9-one (21).¹⁰ ¹H NMR (CDCl₃) δ 4.00 (s, 3H), 6.90 (d, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.39-7.56 (m, 4H), 7.45 (dd, *J* = 7.8, 1.0 Hz, 1H); ¹³C NMR (CDCl₃) 56.56, 109.16, 118.29, 119.83, 125.19, 126.47, 129.91, 131.80, 132.19, 132.99, 135.52, 140.01, 162.39, 180.86; IR (CDCl₃) 3057, 2943, 1639, 1456 cm⁻¹; HRMS *m/z* 242.0404 (calcd for C₁₄H₁₀O₂S, 242.0402).

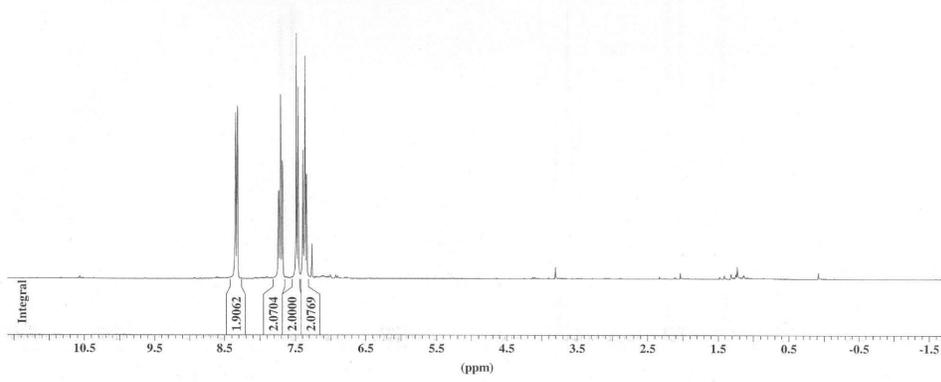
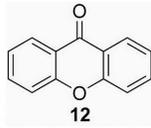
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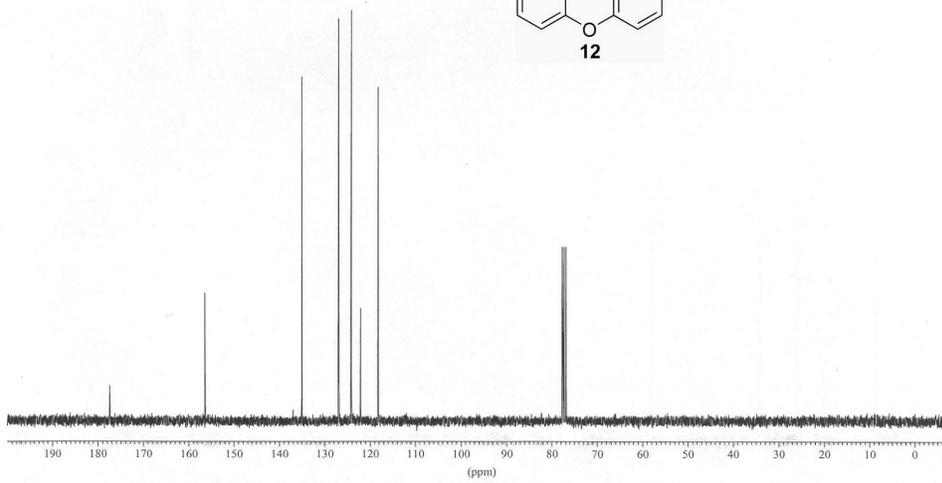
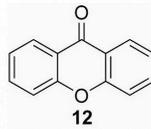
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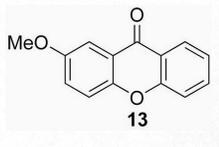
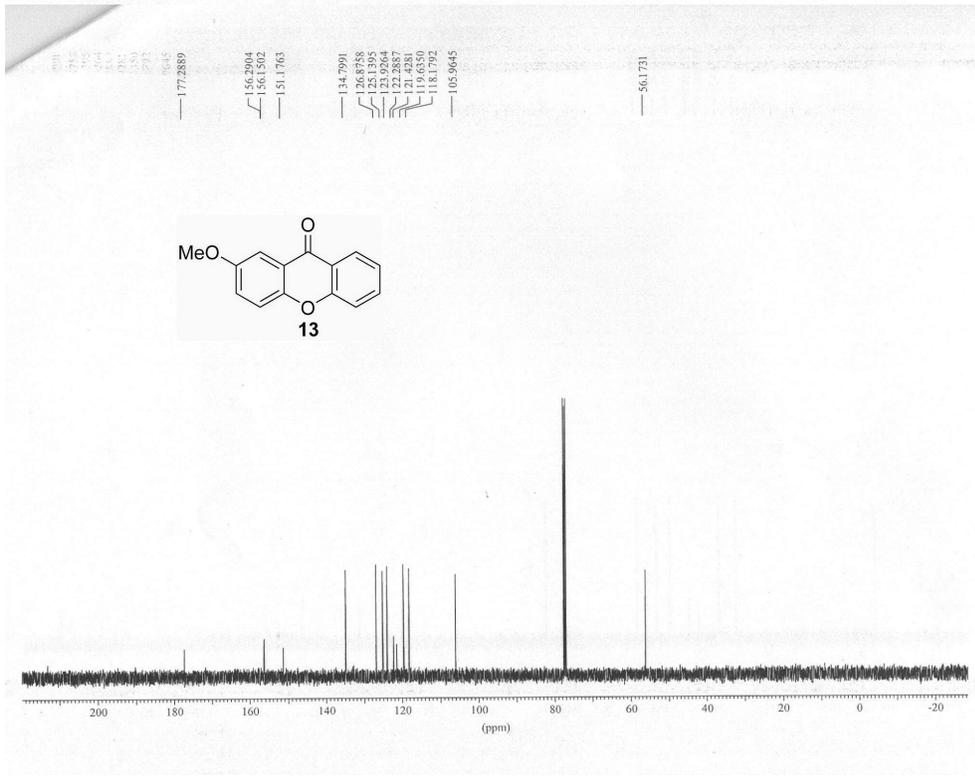
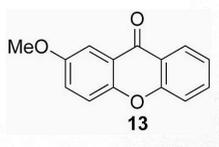
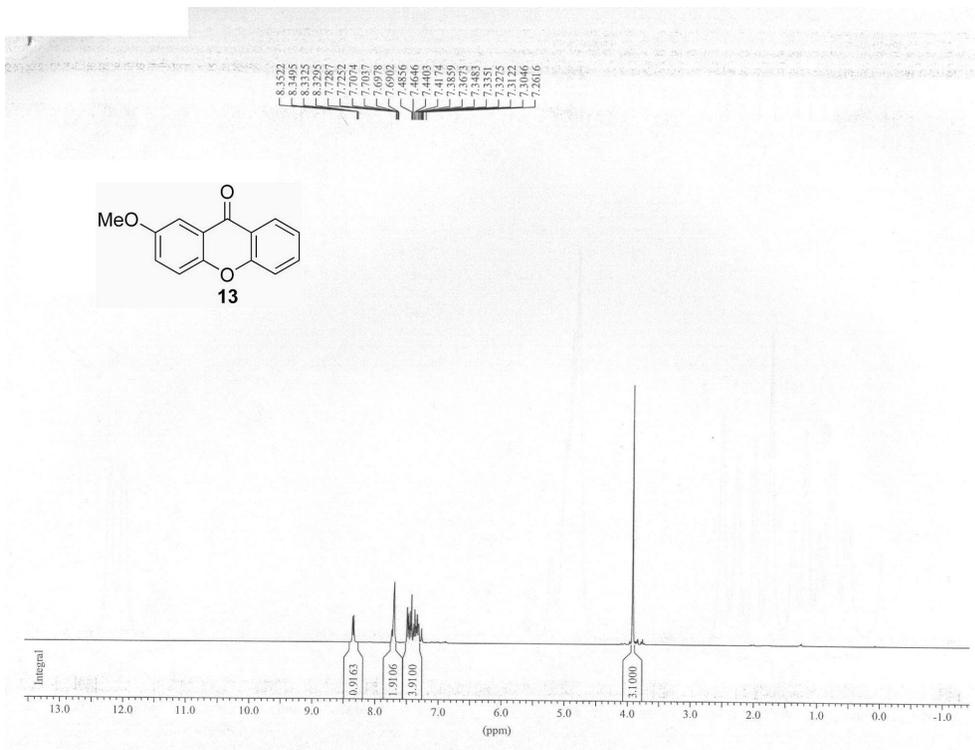
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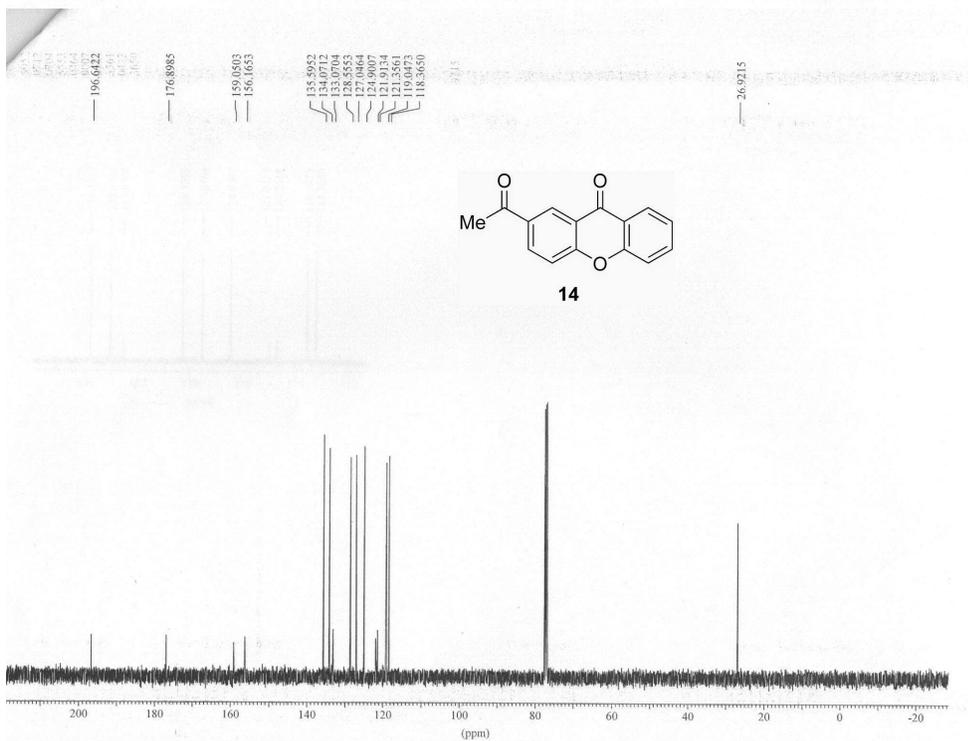
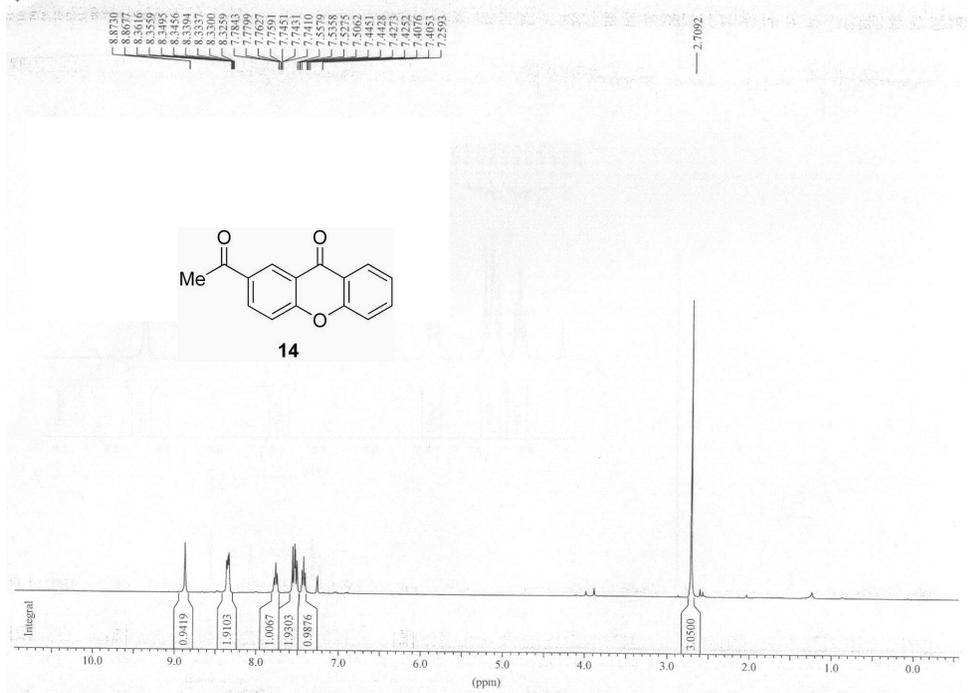
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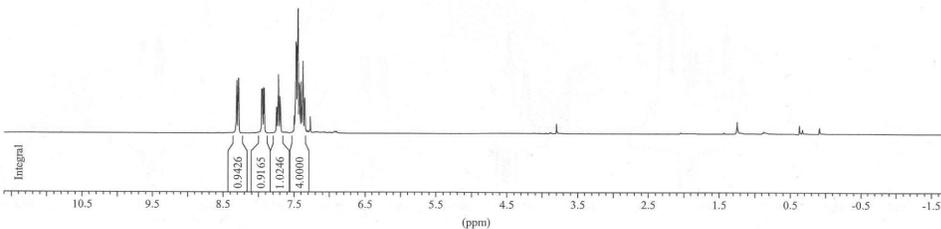
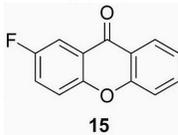




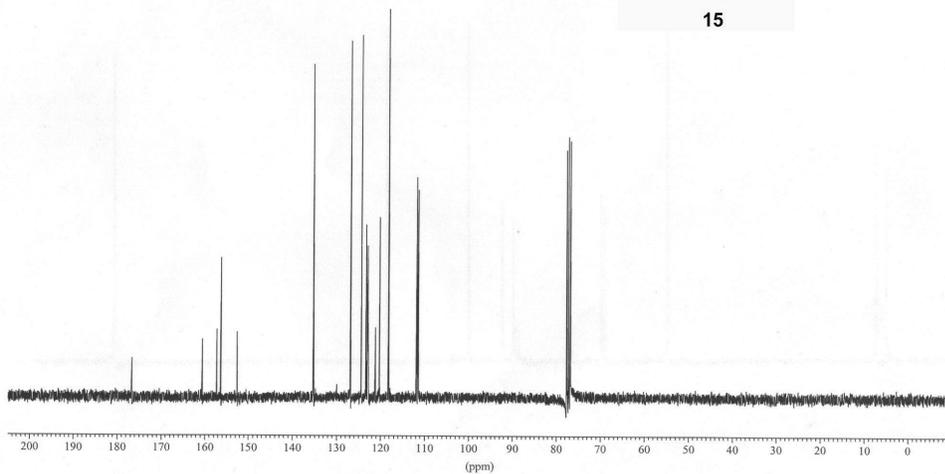
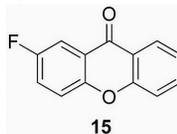


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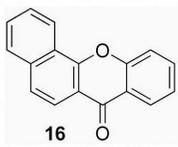
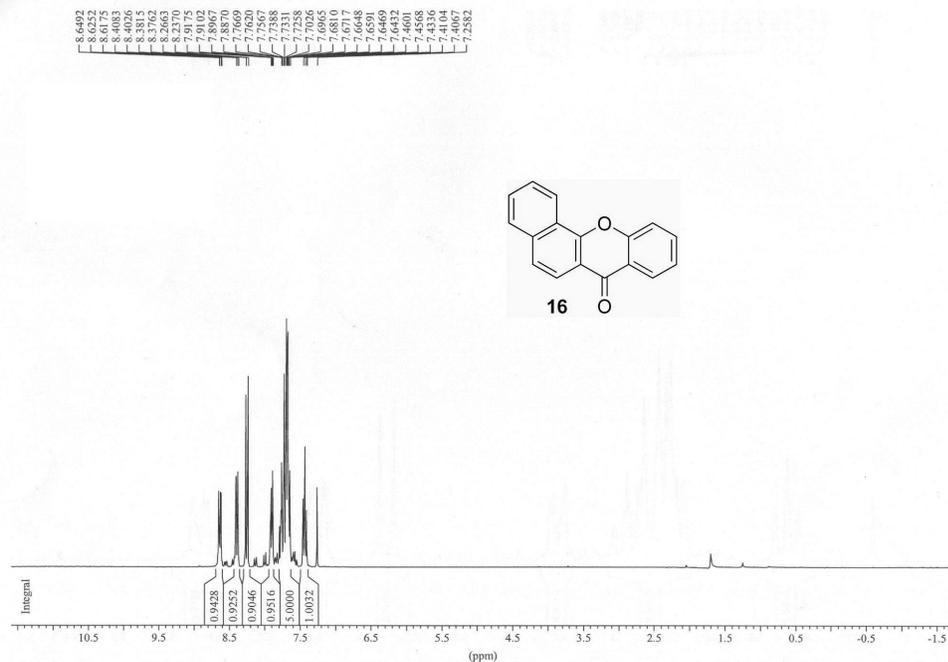
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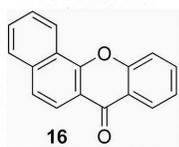
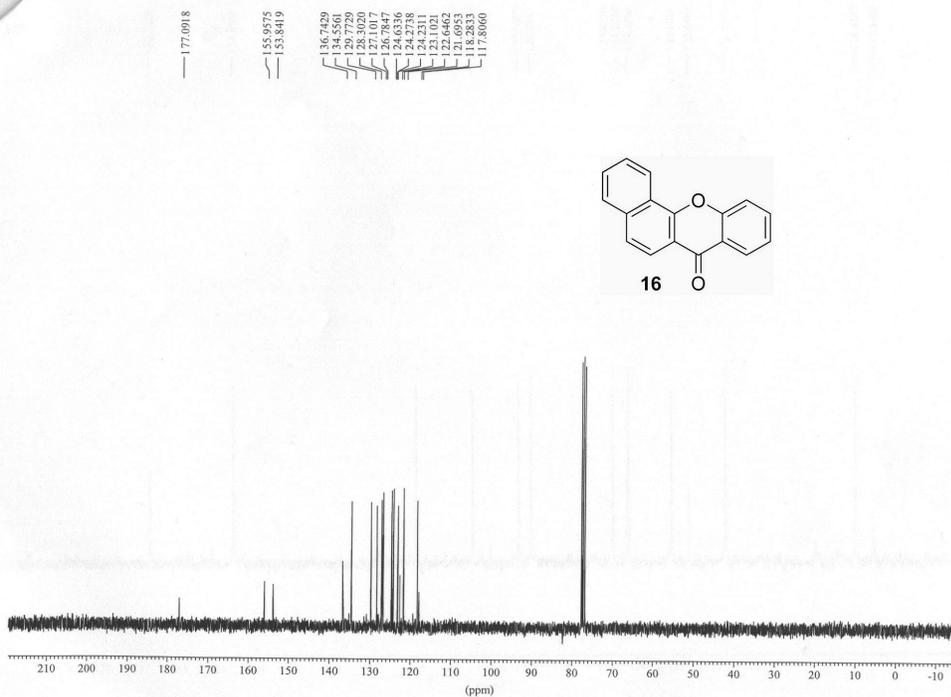
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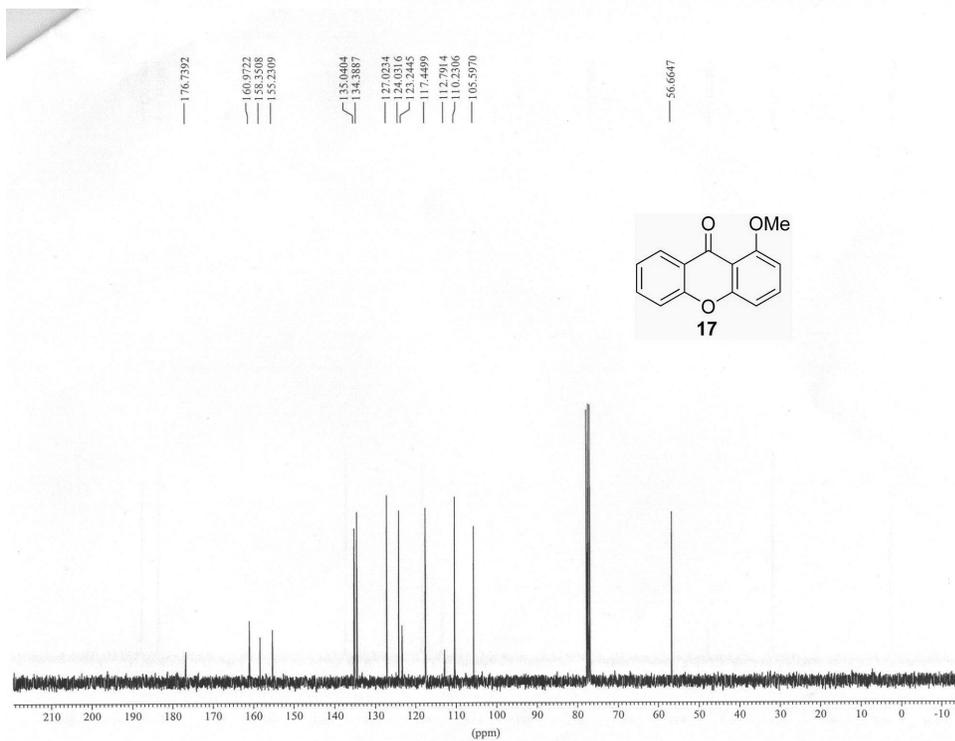
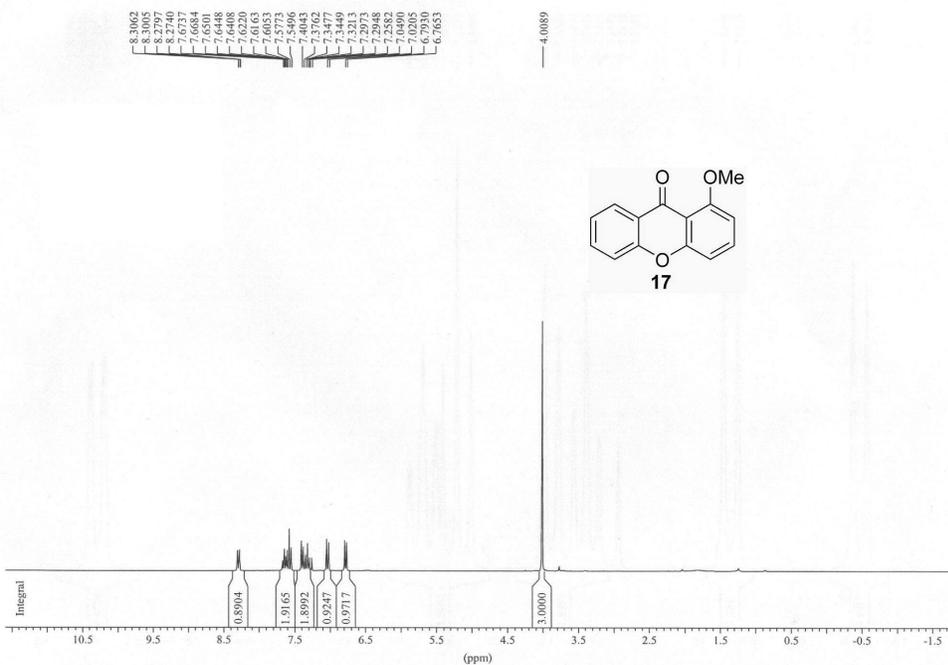


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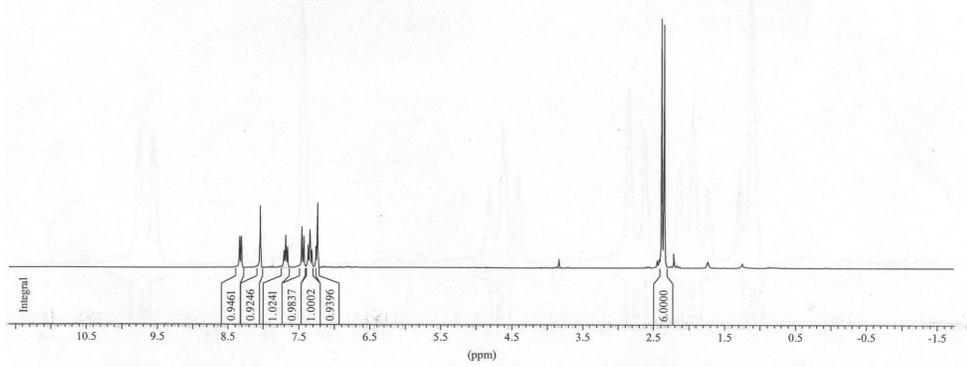
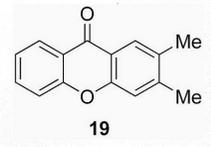




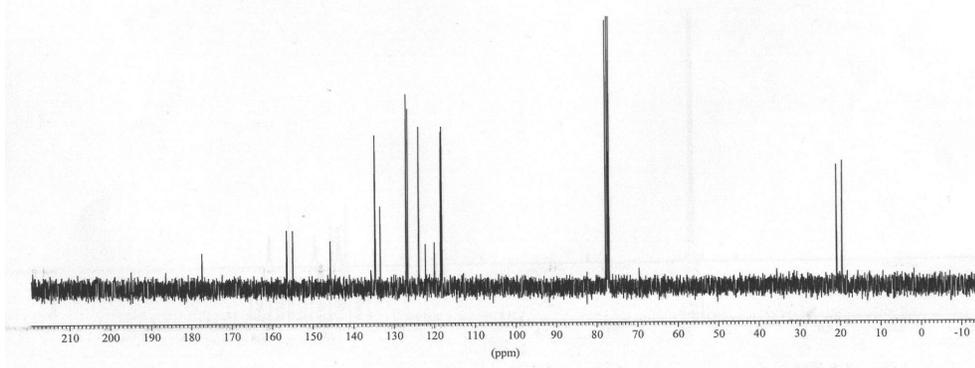
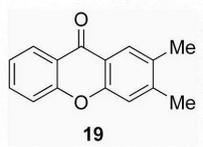
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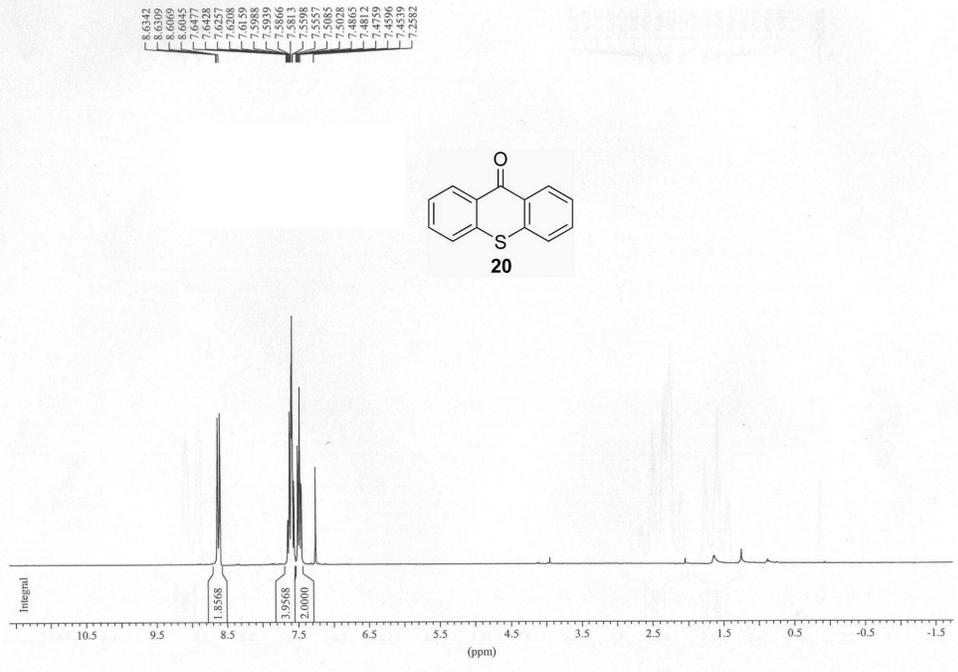


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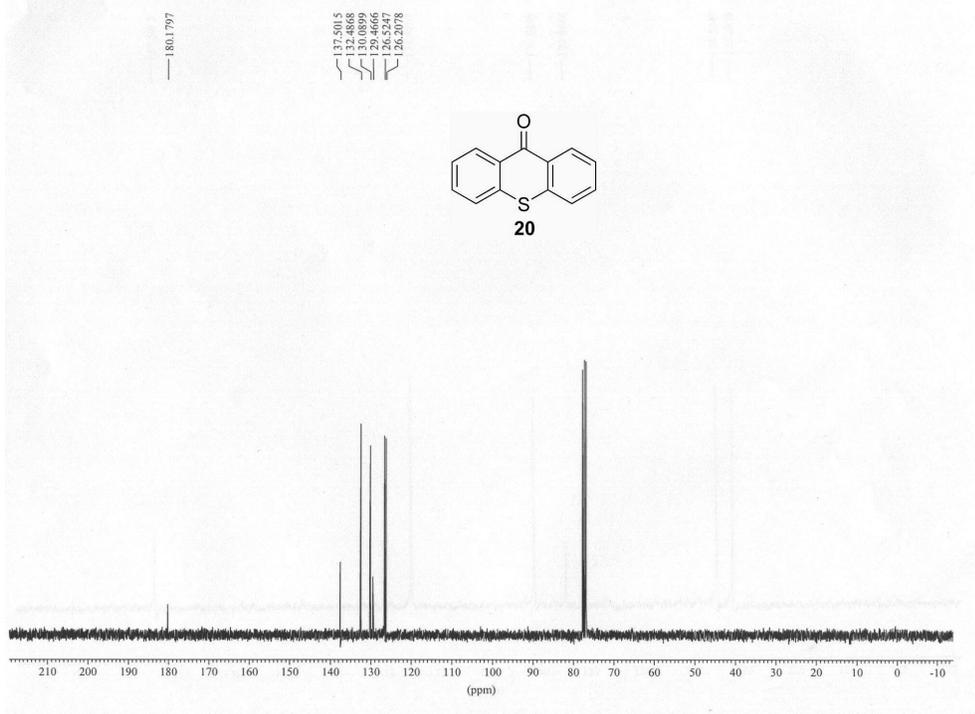


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