Supporting Information

Modular Synthesis of Tetrahydrofluorenones From 5-Alkylidene Meldrum's Acids

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General Considerations: All reactions were carried out under a dry N₂ atmosphere in flame-dried round bottom flasks or oven-dried Schlenk glassware. MeNO₂ was distilled from CaH₂ and stored under N₂ in a Schlenk flask. Dry dichloroethane was dried and purified from a solvent system by the published procedure.¹ BF₃•OEt₂ was distilled under vacuum from CaH₂ through a 15 cm Vigreux column before use. All other commercial reagents were used as received without further purification. 5-(phenylmethylene) Meldrum's acid² (**4h**), 5-[(2-naphthyl)methylene] Meldrum's acid³ (**4g**), and 1-((*E*)-buta-1,3-dienyl)benzene⁴ (**5d**) were prepared according to published procedures. Reactions were monitored using commercial TLC plates visualized under UV light and developed with cerium molybdate (Hanessian's stain). Flash chromatography was performed using 230-400 mesh silica gel. ¹H NMR spectra were referenced to residual CHCl₃ (7.24 ppm); ¹³C NMR spectra were referenced to CDCl₃ (77.0 ppm). ¹³C NMR hydrogen multiplicity was determined by a JMOD experiment for compounds **4a-4f** and **4i-4k**; all others were determined from DEPT-90 and DEPT-135 experiments. High resolution mass spectra were obtained at the University of Waterloo Mass Spectrometry Facility. Melting points are uncorrected.

Preparation of Alkylidene Meldrum's Acids (4a-4f, 4i-4k):

Alkylidene Meldrum's acids were prepared from Knoevenagel condensation of substituted benzaldehydes with Meldrum's acid in water (Method A)^{5,6} or by conjugate addition of the corresponding arylmagnesium bromide² to 5-(1-methoxymethylene) Meldrum's acid⁷ (Method B). All products were recrystallized from MeOH and are bench-stable.

5-[(3,5-Dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4a):

Prepared from 3,5-dimethoxybenzaldehyde and isolated as a yellow powder by Method A. M.p. 156-158 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.31 (s, 1H), 7.26 (d, *J* = 2.2 Hz, 2H), 6.66 (t, *J* = 2.2 Hz, 1H), 3.82 (s, 6H), 1.78 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.3 (C), 160.5 (C), 159.6 (C), 157.9 (CH), 133.1 (C), 115.1 (C), 111.2 (CH), 106.7 (CH), 104.5 (C), 55.5 (CH₃), 27.5 (CH₃); HRMS(EI) *m/z* calcd for C₁₅H₁₆O₆ (M⁺): 292.0947 Found: 292.0939.

5-[(3,4-Dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4b):

Prepared from 3,4-dimethoxybenzaldehyde and isolated as a bright yellow powder by Method A. M.p. 156-158 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.34 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 1.77 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.1 (C), 160.6 (C), 158.2 (CH), 154.7 (C), 148.7 (C), 132.6 (CH), 125.0 (C), 115.6 (CH), 110.6 (C), 110.5 (CH), 104.1 (C), 56.1 (CH₃), 55.9 (CH₃), 27.4 (CH₃); HRMS(EI) *m/z* calcd for C₁₅H₁₆O₆ (M⁺): 292.0947 Found: 292.0940.

5-[(3,4,5-Trimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4c):

Prepared from 3,4,5-trimethoxybenzaldehyde and isolated as a pale yellow powder by Method A. M.p. 155-156 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.30 (s, 1H), 7.59 (s, 2H), 3.96 (s, 3H), 3.89 (s, 6H), 1.77 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.8 (C), 160.2 (C), 158.0 (CH), 152.6 (C), 143.8 (C), 126.6 (C), 112.5 (CH), 112.4 (C), 104.3 (C), 61.1 (CH₃), 56.2 (CH₃), 27.4 (CH₃); HRMS(EI) *m/z* calcd for C₁₆H₁₈O₇ (M⁺): 322.1053 Found: 322.1045.

5-[(3-Methoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4d): Prepared from 3-methoxybenzaldehyde and isolated as an off-white powder by Method A. M.p. 86-88 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.36 (s, 1H), 7.78 (t, *J* = 3.9 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.12-7.08 (m, 1H), 3.84 (s, 3H), 1.78 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.1 (C), 159.6 (C), 159.3 (C), 157.8 (CH), 132.7 (C), 129.5 (CH), 126.8 (CH), 120.4 (CH), 117.0 (CH), 114.8 (C), 104.4 (CH), 55.3 (CH₃), 27.4 (CH₃); HRMS(EI) *m/z* calcd for C₁₄H₁₄O₅ (M⁺): 262.0841 Found: 262.0847.

5-[(2,3-Dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4e):

Prepared from 2,3-dimethoxybenzaldehyde and isolated as a bright yellow powder by Method A. M.p. 104-105 °C [lit. M.p.⁸ 98-100 °C (EtOAc)] ; ¹H NMR (CDCl₃, 300 MHz) δ 8.67 (s, 1H), 7.48-7.44 (m, 1H), 7.10-7.04 (m, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 1.79 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 162.8 (C), 159.6 (C), 153.1 (CH), 152.3 (C),

149.7 (C), 126.3 (C), 123.5 (CH), 123.0 (CH), 117.0 (CH), 116.4 (C), 104.5 (C), 61.8 (CH₃), 55.9 (CH₃), 27.6 (CH₃); HRMS(EI) *m/z* calcd for C₁₅H₁₆O₆ (M⁺): 292.0947 Found: 292.0939.

5-[(4-Bromo-3,5-dimethoxyphenyl)]-2,2-dimethyl-1,3-dioxane-4,6-dione (4f):

Prepared from 4-bromo-3,5-dimethoxybenzaldehyde⁹ and isolated as a yellow powder by Method A. M.p. 187-189 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.32 (s, 1H), 7.46 (s, 2H), 3.94 (s, 6H), 1.79 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.3 (C), 159.8 (C), 157.3 (CH), 157.0 (C), 131.3 (C), 114.8 (CH), 110.1 (C), 108.5 (C), 104.6 (C) 55.6 (CH₃), 27.5 (CH₃); HRMS(EI) *m/z* calcd for C₁₅H₁₅BrO₆ (M⁺): 370.0052 Found: 370.0041.

5-[(4-Methoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4i)⁵: Prepared from 4-methoxybenzaldehyde and isolated as a yellow powder by Method A. M.p. 125-126 °C [lit. m.p.¹⁰ 122-124 °C ; ¹H NMR (CDCl₃, 300 MHz) δ 8.36 (s, 1H), 8.21 (d, *J*= 9.0 Hz, 2H), 6.96 (d, *J*= 9.0 Hz, 2H), 3.89 (s, 3H), 1.77 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.6 (C), 164.0 (C), 160.4 (C), 157.9 (C), 137.6 (CH), 124.7 (C), 114.3 (CH), 110.8 (C), 104.1 (C), 55.6 (CH₃), 27.6 (CH₃); HRMS(EI) *m/z* calcd for C₁₄H₁₄O₅ (M⁺): 262.0841 Found: 262.0841

5-[(3-Chlorophenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4j)¹¹: Prepared from 3-chlorophenylmagnesium bromide and isolated as an off-white powder by Method B. M.p. 115-116 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.32 (s, 1H), 8.02 (s, 1H), 7.85 (d, *J*= 7.8 Hz, 1H), 7.50 (d, *J*= 8.3 Hz, 1H), 7.29 (t, *J*= 7.9 Hz, 1H), 1.79 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 162.7 (C), 159.3 (C), 156.0 (CH), 134.6 (C), 133.2 (C), 133.1 (CH), 132.5 (CH), 131.3 (CH), 129.8 (CH), 116.2 (C), 104.7 (C), 27.6 (CH₃); HRMS(EI) *m/z* calcd for C₁₃H₁₁ClO₄ (M⁺): 266.0346 Found: 266.0341.

5-[(4-Chlorophenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4k)¹¹: Prepared from 4-chlorophenylmagnesium bromide and isolated as an off-white powder by Method B. M.p. 157-158 °C [lit m.p.¹² 161-162 °C]; ¹H NMR (CDCl₃, 300 MHz) δ 8.35 (s, 1H), 8.01 (d, *J*= 8.5 Hz, 2H), 7.43 (d, *J*= 8.6 Hz, 2H), 1.79 (s, 6H); ¹³C NMR (CDCl₃, 75

MHz) δ 163.0 (C), 159.6 (C), 156.4 (CH), 140.1 (C), 134.9 (CH), 130.0 (C), 129.1 (CH), 115.0 (C), 104.7 (C), 27.6 (CH₃); HRMS(EI) m/z calcd for C₁₃H₁₁ClO₄ (M⁺): 266.0346 Found: 266.0353.

Preparation of Diels-Alder Cycloadducts (6a-6c):

Meldrum's Acid 4a + Butadiene Sulphone 5a: An oven-dried Schlenk tube cooled under N₂ was charged with alkylidene Meldrum's acid **4a** (2.0 g, 6.8 mmol, 1 equiv), butadiene sulphone (8.0 g, 68 mmol, 10 equiv), and MeNO₂ (34 mL, 0.2 M). The tube was heated in an oil bath at 100 °C for 16 hours, cooled to rt, poured into saturated NaHCO₃ solution and stirred until bubbling ceased. This was extracted with EtOAc (2X), and the combined organic layers were washed with water (1X) and brine (1X), dried over MgSO₄, filtered and concentrated. The product **6a** was isolated as a white solid in 82% yield after purification by flash chromatography eluting with 3:17 EtOAc:hexanes. M.p. 118-119 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.34 (m, 3H), 6.01-5.96 (m, 1H), 5.74-5.69 (m, 1H), 3.72 (s, 6H), 3.47 (dd, J = 11.7 Hz, 5.1 Hz, 1H), 2.99-2.83 (m, 2H), 2.48 (dd, J = 17.9 Hz, 4.6 Hz, 1H), 2.34 (dt, J = 17.8 Hz, 4.7 Hz, 1H), 1.58 (s, 3H), 1.06 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.7 (C), 166.9 (C), 160.8 (C), 141.5 (C), 127.0 (CH), 121.0 (C), 106.7 (CH), 104.9 (C), 100.2 (CH), 55.3 (CH₃), 52.5 (C), 46.3 (CH), 34.8 (CH₂), 29.8 (CH₃), 28.8 (CH₂), 27.9 (CH₃); HRMS(EI) m/z calcd for C₁₉H₂₂O₆ (M⁺): 346.1416 Found: 346.1420.

Meldrum's Acid 4a + 2,3-dimethylbutadiene 5b: An oven-dried Schlenk tube cooled under N₂ was charged with alkylidene Meldrum's acid **4a** (200 mg, 0.68 mmol, 1 equiv) and 2,3-dimethylbutadiene (42 μ L, 0.75 mmol, 1.1 equiv) was added to the top chamber via syringe and washed into the tube with MeNO₂ (3.4 mL, 0.2 M). The tube was heated in an oil bath at 100 °C for 16 hours, cooled to rt, and the contents transferred into a

round bottom flask with EtOAc. The solvent was removed by rotary evaporation, and the product **6b** isolated as a white solid in quantitative yield after drying under high vacuum. M.p. 129-130 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.35 (d, *J* = 2.1 Hz, 2H), 6.32 (t, *J* = 2.1 Hz, 1H), 3.72 (s, 6H), 3.48 (dd, *J* = 12.0 Hz, 5.4 Hz, 1H), 2.94-2.89 (m, 2H), 2.29 (d, *J* = 17.4 Hz, 1H), 2.15 (dd, *J* = 17.4 Hz, 5.3 Hz, 1H), 1.73 (s, 3H), 1.66 (s, 3H), 1.58 (s, 3H), 1.04 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 171.1 (C), 167.0 (C), 160.9 (C), 141.7 (C), 126.2 (C), 119.8 (C), 106.7 (CH), 104.8 (C), 100.2 (CH), 55.4 (CH₃), 53.9 (C), 47.0 (CH), 40.8 (CH₂), 35.0 (CH₂), 29.8 (CH₃), 28.0 (CH₃), 19.0 (CH₃), 18.3 (CH₃); HRMS(EI) *m/z* calcd for C₂₁H₂₆O₆ (M⁺): 374.1729 Found: 374.1725.

Meldrum's Acid 4a + 1-((*E*)-Buta-1,3-dienyl)benzene 5e: An oven-dried Schlenk flask cooled under N₂ was charged with Meldrum's acid **4a** (3.06 g, 105 mmol, 1.0 equiv). The diene (1.5 g, 115 mmol, 1.1 equiv) was added to the chamber and washed into the flask with (CH₂Cl)₂ (52 mL, 0.2 M). The flask was sealed, heated to 100 °C for 16 hours, then cooled to rt. The solution was rinsed into a flask with EtOAc and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with 1:4 EtOAc:hexanes. The endo adduct **6c** eluted first, and was isolated as a white powder. M.p. 167-169 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.31-7.18 (m, 5H), 6.40 (d, *J* = 2.2 Hz, 2H), 6.33 (d, *J* = 2.2 Hz, 1H), 6.15-6.11 (m, 1H), 5.81 (dd, *J* = 10.2 Hz, 2.0 Hz, 1H), 4.50 (br s, 1H), 3.83-3.72 (m, 1H), 3.72 (s, 6H), 3.06-2.95 (m, 1H), 2.47 (dt, *J* = 18.3 Hz, 5.2 Hz, 1H), 0.76 (s, 3H), 0.58 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.5 (C), 163.8 (C), 160.9 (C), 141.2 (C), 138.8 (C), 129.5 (CH), 128.8 (CH), 128.02 (CH), 127.98 (CH), 126.3 (CH), 106.8 (CH), 105.5 (C), 100.4 (CH), 59.8 (C), 55.3 (CH₃), 50.7 (CH), 47.8 (CH), 29.4 (CH₂), 28.6 (CH₃), 28.5 (CH₃); HRMS(EI) *m/z* calcd for C₂₅H₂₆O₆ (M⁺): 422.1729 Found: 422.1736. The exo adduct **6c** eluted second, and was isolated as a white powder. M.p. 148-150 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.32-7.23 (m, 5H), 6.45 (d, *J* = 2.2 Hz, 2H), 6.30 (d, *J* = 2.2 Hz, 1H), 6.26-6.20 (m, 1H), 5.81 (doublet of quintets, *J* = 10.2 Hz, 2.0 Hz, 1H), 3.98 (app d, *J* = 2.0 Hz, 1H), 3.70 (s, 6H), 3.56 (dd, *J* = 9.5 Hz, 6.3 Hz, 1H), 3.01-2.90 (m, 1H), 2.65-2.55 (m, 1H), 1.49 (s, 3H), 1.15 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.7 (C), 166.3 (C), 160.7 (C), 142.7 (C), 138.6 (C), 130.0 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 125.0 (CH), 107.6 (CH), 104.9 (C), 99.9 (CH), 59.7

(C), 55.3 (CH₃), 48.9 (CH), 41.8 (CH), 30.0 (CH₂), 29.3 (CH₃), 28.8 (CH₃); HRMS(EI) *m/z*. calcd for C₂₅H₂₆O₆ (M⁺): 422.1729 Found: 422.1716.

Crystals of endo adduct **6c** suitable for X-ray crystallography were obtained by slow evaporation of a saturated EtOH solution.

The stereochemistry of the two adducts was assigned based on the following data: a) NOESY correlations detailed in Table 1 and b) the strong anisotropic shielding of the Meldrum's acid methyl signals in the endo adduct (0.76 and 0.58 ppm) vs that found in the exo adduct (1.49 and 1.15 ppm) c) The X-ray crystal structure of endo **6c** (see attached CIF file)

Endo adduct **6c**

Exo adduct **6c**

Proton (δ)	nOe w/ proton (δ)	Proton (δ)	nOe w/ proton (δ)
H _b (4.50)	H _a (3.83-3.72), H _e (7.31-7.18), H _f (5.81)	H _a (3.56)	H _c (6.45), H _e (7.32-7.23), H _g (2.65-2.55)
Me ₁ (0.76)	H _c (6.33), H _d (6.33), Me ₂ (0.58), Me ₃ (3.72)	H _b (3.98)	H _e (7.32-7.23), H _f (5.81), Me ₂ (1.49)
Me ₂ (0.58)	H _e (7.31-7.18), Me ₁ (0.76)	Me ₁ (1.15)	H _c (6.45), Me ₂ (1.50)
		Me ₂ (1.49)	H _b (3.98), Me ₁ (1.15)

Table 1. NOESY correlations of endo adduct **6c** and exo adduct **6c** relevant to the assignment of relative stereochemistry

Synthesis of Tetrahydrofluorenones **7a-7b** from Cycloadducts **6a-6b**:

Cycloadduct 5a + TMSOTf: An oven-dried Schlenk tube cooled under N₂ was charged with cycloadduct **5a** (100 mg, 0.29 mmol, 1.0 equiv). A solution of TMSOTf in MeNO₂ (0.1 equiv/100 μ l) was washed into the tube with MeNO₂ (2.8 mL, 0.1 M) and the tube was sealed and heated to 100 °C for 2.5 hours. Once the reaction had cooled to rt., the contents were rinsed into a separatory funnel with EtOAc and washed with water followed by brine. The organic layer was dried over MgSO₄, filtered, concentrated *in vacuo*, and purified by flash chromatography eluting with 1:2 EtOAc:hexanes to yield the product as a clear, colourless oil in 85% yield. **(4bR*,8aS*)-4b,5,8,8a-tetrahydro-1,3-dimethoxyfluoren-9-one (7a):** ¹H NMR (CDCl₃, 300 MHz) δ 6.46 (d, *J* = 1.1 Hz, 1H), 6.25 (d, *J* = 1.6 Hz, 1H), 5.85-5.80 (m, 1H), 5.73-5.68 (m, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.46 (dt, *J* = 12.3 Hz, 7.4 Hz, 1H), 3.46 (dt, *J* = 12.2 Hz, 7.9 Hz, 1H), 2.52-2.42 (m, 2H), 2.33-2.29 (m, 1H), 2.17 (dt, *J* = 15.3 Hz, 5.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.7 (C), 167.1 (C), 163.7 (C), 158.8 (C), 128.5 (CH), 126.9 (CH), 119.6 (C), 100.5 (CH), 97.3 (CH), 55.66 (CH₃), 55.63 (CH₃), 46.8 (CH), 37.6 (CH), 28.5 (CH₂), 24.5 (CH₂); HRMS(EI) *m/z* calcd for C₁₅H₁₆O₃ (M⁺): 244.1099 Found: 244.1102.

Cycloadduct 5b + BF₃•OEt₂: An oven-dried Schlenk tube cooled under N₂ was charged with cycloadduct **5b** (100 mg, 0.27 mmol, 1.0 equiv). A solution of BF₃•OEt₂ in (CH₂Cl)₂ (0.1 equiv/100 μ l) was washed into the tube with (CH₂Cl)₂ (2.6 mL, 0.1 M) and the tube was sealed and heated to 100 °C for 30 minutes. The contents were rinsed into a separatory funnel with CH₂Cl₂ and washed with brine (1X). The organic layer was dried over MgSO₄, filtered, concentrated *in vacuo*, and purified by flash chromatography to yield the product as a white solid in 91% yield. **(4aR*,9aS*)-1,4,4a,9a-tetrahydro-6,8-dimethoxy-2,3-dimethylfluoren-9-one (7b):** M.p. 99-100 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.45 (d, *J* = 0.7 Hz, 1H), 6.22 (d, *J* = 1.0 Hz, 1H), 3.829 (s, 3H), 3.827 (s, 3H), 3.38 (dd, *J* = 7.4 Hz, 4.4 Hz, 1H), 2.73 (dt, *J* = 7.9 Hz, 4.5 Hz, 1H), 2.41 (dd, *J* = 8.7 Hz, 4.1 Hz, 1H), 2.29 (ABX, *J* = 8.9 Hz, 2.7 Hz, 1H), 2.21 (ABX, *J* = 8.9 Hz, 4.3 Hz, 1H),

2.05 (dd, $J = 8.8$ Hz, 2.7 Hz, 1H), 1.58 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 204.9 (C), 166.8 (C), 163.6 (C), 158.6 (C), 127.3 (C), 125.6 (C), 119.9 (C), 100.3 (CH), 97.2 (CH), 55.62 (CH_3), 55.58 (CH_3), 47.5 (CH), 38.3 (CH), 35.5 (CH_2), 31.5 (CH_2), 19.3 (CH_3), 19.1 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$ (M^+): 272.1412 Found: 272.1404.

Synthesis of Tetrahydrofluorenones **7a-7c**, **7l-n**:

General Procedure A: An oven-dried Schlenk tube cooled under N_2 was charged with Meldrum's acid alkylidene (200 mg, 1.0 equiv) and the diene (1.1 equiv) was washed into the tube with $(\text{CH}_2\text{Cl}_2)_2$ (0.2 M relative to the alkylidene). The tube was sealed, heated in an oil bath at 100°C for 16 hours, and removed from the bath to cool to rt. A 50 μL aliquot was removed and concentrated to determine conversion and endo:exo ratio (where applicable) of the Diels-Alder reaction by ^1H NMR. A solution of $\text{BF}_3 \cdot \text{OEt}_2$ in $(\text{CH}_2\text{Cl}_2)_2$ (0.1 equiv/100 μL) was washed into the tube with sufficient $(\text{CH}_2\text{Cl}_2)_2$ to bring the total concentration to 0.15 M. The tube was reheated to 100°C for 30 minutes, cooled to rt, and the contents transferred into a separatory funnel with CH_2Cl_2 (*Caution: A small amount of pressure builds up in the tube during the FC acylation as CO_2 is evolved*). The organic phase was washed with brine, dried over MgSO_4 , filtered, and concentrated. Purification by flash chromatography eluting with EtOAc:hexanes solvent mixtures yielded the product.

All reactions were performed according to Procedure A unless noted otherwise.

Meldrum's Acid **4a + Butadiene sulphone **5a**:** 5 equiv of diene was used and the product **7a** isolated as a clear, colourless oil by flash chromatography eluting with 3:7 EtOAc:hexanes in 84% yield. Spectral data were identical to those obtained above.

Meldrum's Acid **4a + 2,3-Dimethylbutadiene **5b**:** The fluorenone **7b** was isolated as a yellow oil by flash chromatography eluting with 1:4 EtOAc:hexanes in 86% yield. The

oil solidified upon two weeks storage at rt in air, with no change in the NMR spectra. Spectral data were identical to those obtained above.

Meldrum's Acid 4a + Isoprene 5c: By analysis of the crude NMR after the DA reaction, the adduct was formed as 9:1 mixture of regioisomers. After the FC reaction, only the major product could be isolated by flash chromatography eluting with 1:9 to 1:4 EtOAc:hexanes as a yellow oil in 74% yield. **(4aR*,9aS*)-1,4,4a,9a-Tetrahydro-6,8-dimethoxy-3-methylfluoren-9-one (7c):** ^1H NMR (CDCl_3 , 300 MHz) δ 6.47 (d, J = 1.3 Hz, 1H), 6.25 (d, J = 1.7 Hz, 1H), 5.46 (dd, J = 5.7 Hz, 4.2 Hz, 1H), 3.84 (s, 6H), 3.47 (dd, J = 7.3 Hz, 4.8 Hz, 1H), 2.76 (dt, J = 4.5 Hz, 2.9 Hz, 1H), 2.46-2.36 (m, 2H), 2.27-2.18 (m, 1H), 2.09 (dd, J = 14.9 Hz, 4.6 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.1 (C), 167.0 (C), 163.6 (C), 158.8 (C), 135.1 (C), 121.0 (CH), 119.8 (C), 100.4 (CH), 97.2 (CH), 55.7 (CH_3), 46.8 (CH), 38.0 (CH), 33.7 (CH_2), 25.1 (CH_2), 23.6 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$ (M^+): 258.1256 Found: 258.1255.

Meldrum's Acid 4a + 1-((E)-Buta-1,3-dienyl)benzene 5e: By analysis of the crude NMR after the DA reaction, the adduct was formed in a 67:33 exo:endo ratio. After treatment with $\text{BF}_3 \cdot \text{OEt}_2$, and flash chromatography eluting with 1:4 EtOAc:hexanes, the endo adduct **6c** eluted first and was isolated as a white powder in 29% yield. Spectral data were identical to those obtained above. The fluorenone **7l** eluted second, and was isolated as a clear, colourless oil in 53% yield. **(1R*,4aR*,9aR*)-1,4,4a,9a-Tetrahydro-6,8-dimethoxy-1-phenylfluoren-9-one (7l):** ^1H NMR (CDCl_3 , 300 MHz) δ 7.37-7.27 (m, 4H), 7.22-7.19 (m, 1H), 6.48 (d, J = 1.5 Hz, 1H), 6.29 (d, J = 1.8 Hz, 1H), 6.00-5.94 (m, 1H), 5.89-5.84 (m, 1H), 4.05 (br s, 1H), 3.88-3.80 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.49 (dd, J = 13.6 Hz, 7.8 Hz, 1H), 3.00 (dd, J = 7.8 Hz, 3.2 Hz, 1H), 2.63-2.55 (m, 1H), 2.09 (dt, J = 14.7 Hz, 4.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 202.4 (C), 167.0 (C), 163.4 (C), 159.0 (C), 144.5 (C), 130.9 (CH), 128.4 (CH), 127.7 (CH), 126.3 (CH), 125.9 (CH), 118.1 (C), 100.6 (CH), 97.4 (CH), 55.6 (CH_3), 54.9 (CH), 40.0 (CH), 36.5 (CH), 29.4 (CH_2); HRMS(EI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3$ (M^+): 320.1412 Found: 320.1416.

Meldrum's acid 4a + *trans*-1,3-pentadiene 5f: By analysis of the crude NMR after the DA reaction, the adduct was formed as a 64:36 *exo:endo* ratio. After treatment with $\text{BF}_3 \cdot \text{OEt}_2$, and flash chromatography eluting with 3:17 EtOAc:hexanes, the *endo* adduct **6d** eluted first and was isolated as a white powder in 4% yield. M.p. 209-211 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 6.39 (d, J = 2.2 Hz, 2H), 6.32 (t, J = 2.2 Hz, 1H), 5.96-5.90 (m, 1H), 5.48 (dd, J = 10.2 Hz, 2.1 Hz, 1H), 3.73 (s, 6H), 3.59 (dd, J = 11.8 Hz, 5.6 Hz, 1H), 3.23 (br s, 1H), 2.95-2.85 (m, 1H), 2.35 (dt, J = 18.2 Hz, 5.3 Hz, 1H), 1.56 (s, 3H), 1.07 (d, J = 7.4 Hz, 3H), 0.80 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 170.3 (C), 164.5 (C), 161.0 (C), 142.0 (C), 127.7 (CH), 126.4 (CH), 107.1 (CH), 105.7 (C), 100.3 (CH), 58.7 (C), 55.4 (CH_3), 46.2 (CH), 41.0 (CH), 29.6 (CH_3), 29.2 (CH_2), 28.9 (CH_3), 16.9 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6$ (M^+): 360.1573 Found: 360.1583.

Increasing the polarity of the mobile phase to 1:4 EtOAc:hexanes and continued elution yielded a large number of mixed fractions containing both **7m** and **7n** which were combined to give a 83% yield. Repurification of the isomers by flash chromatography eluting with 1:4 EtOAc:hexanes yielded first the minor isomer as a white powder in 14% yield. (**1S*,4aR*,9aS***)-**1,4,4a,9a-tetrahydro-6,8-dimethoxy-1-methylfluoren-9-one (7n)**: M.p. 140-142 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 6.44 (s, 1H), 6.29 (s, 1H), 5.74 (dt, J = 9.8 Hz, 2.6 Hz, 1H), 5.58 (br d, J = 10.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.98-2.89 (m, 1H), 2.69-2.57 (m, 2H), 2.26-2.16 (m, 1H), 2.06 (dd, J = 10.6 Hz, 9.6 Hz, 1H), 1.32 (d, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 201.4 (C), 166.5 (C), 158.9 (C), 157.8 (C), 136.1 (CH), 125.1 (CH), 118.6 (C), 99.7 (CH), 97.2 (CH), 59.1 (CH), 55.7 (CH_3), 41.0 (CH), 32.7 (CH), 29.0 (CH_2), 19.4 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3$ (M^+): 258.1256 Found: 258.1255.

The major isomer eluted second and was isolated a white powder in 39% yield (**1R*,4aR*,9aS***)-**1,4,4a,9a-tetrahydro-6,8-dimethoxy-1-methylfluoren-9-one (7m)**: M.p. 63-64 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 6.46 (d, J = 0.9 Hz, 1H), 6.27 (s, 1H), 5.73 (br s, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.38 (dd, J = 14.9 Hz, 7.4 Hz, 1H), 2.70-2.58 (m, 1H), 2.54-2.41 (m, 1H), 1.94-1.87 (m, 1H), 1.31 (d, J = 6.9 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 204.0 (C), 167.0 (C), 163.4 (C), 159.1 (C), 135.1 (CH), 125.5 (CH), 118.8 (C), 100.5 (CH), 97.4 (CH), 55.70 (CH_3), 55.66 (CH_3), 54.2 (CH), 37.7 (CH), 30.5 (CH),

28.9 (CH₂), 20.5 (CH₃); HRMS(EI) *m/z* calcd for C₁₆H₁₈O₃ (M⁺): 258.1256 Found: 258.1265.

Synthesis of Tetrahydrofluorenones 7d-7g:

All reactions were performed according to Procedure A

Meldrum's Acid 4b + 2,3-Dimethylbutadiene 5b: Isolated by flash chromatography eluting with 1:4 EtOAc:hexanes as a white solid in 76% yield. **(4aR*,9aS*)-1,4,4a,9a-Tetrahydro-6,7-dimethoxy-2,3-dimethylfluoren-9-one (7d):** M.p. 102-104 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.09 (s, 1H), 6.88 (s, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 3.49 (dt, *J*= 7.0 Hz, 4.6 Hz, 1H), 2.80 (dt, *J*= 7.1 Hz, 4.8 Hz, 1H), 2.47 (dd, *J*= 14.3 Hz, 6.7 Hz, 1H), 2.34 (ABX, *J*= 14.8 Hz, 4.9 Hz, 1H), 2.27 (ABX, *J*= 14.8 Hz, 6.7 Hz, 1H), 2.09 (dd, *J*= 14.5 Hz, 4.4 Hz, 1H), 1.61 (s, 3H), 1.48 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 207.9 (C), 155.5 (C), 153.7 (C), 149.4 (C), 130.5 (C), 127.3 (C), 125.9 (C), 106.0 (CH), 103.6 (CH), 56.2 (CH₃), 56.0 (CH₃), 47.4 (CH), 38.3 (CH), 35.6 (CH₂), 31.7 (CH₂), 19.5 (CH₃), 19.2 (CH₃); HRMS(EI) *m/z* calcd for C₁₇H₂₀O₃ (M⁺): 272.1412 Found: 272.1409.

Meldrum's Acid 4c + 2,3-Dimethylbutadiene 5b: Isolated by flash chromatography eluting with 1:4 EtOAc:hexanes as a clear, colourless oil in 90% yield. **(4aR*,9aS*)-1,4,4a,9a-Tetrahydro-6,7,8-trimethoxy-2,3-dimethylfluoren-9-one (7e):** ¹H NMR (CDCl₃, 300 MHz) δ 6.65 (s, 1H), 3.98 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 3.42 (dd, *J*= 7.3 Hz, 4.8 Hz, 1H), 2.76 (dt, *J*= 7.5 Hz, 4.9 Hz, 1H), 2.47 (dd, *J*= 14.6 Hz, 6.7 Hz, 1H), 2.32 (ABX, *J*= 14.8 Hz, 4.7 Hz, 1H), 2.23 (ABX, *J*= 14.9 Hz, 7.1 Hz, 1H), 2.05 (dd, *J*= 14.6, 4.7 Hz), 1.61 (s, 3H), 1.50 (s, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.1 (C), 159.6 (C), 156.6 (C), 150.8 (C), 140.5 (C), 127.3 (C), 125.8 (C), 123.3 (C), 102.2 (CH), 61.8 (CH₃), 61.3 (CH₃), 56.2 (CH₃), 47.7 (CH), 38.2 (CH), 35.8 (CH₂), 31.6 (CH₂), 19.4 (CH₃), 19.2 (CH₃); HRMS(EI) *m/z* calcd for C₁₈H₂₂O₄ (M⁺): 302.1518 Found: 302.1512.

Meldrum's Acid 4d + 2,3-Dimethylbutadiene 5b: Prepared by procedure A; by analysis of the crude ^1H NMR, the product was formed as a 67:33 para:ortho mixture. Flash chromatography eluting with 1:4 EtOAc:hexanes yielded first the para isomer as a white solid in 46% yield. **(4aR*,9aS*)-1,4,4a,9a-Tetrahydro-6-methoxy-2,3-dimethylfluoren-9-one (7f):** M.p. 116-118 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 7.60 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 1.8 Hz, 1H), 6.85 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 3.86 (s, 3H), 3.50 (dd, J = 7.3 Hz, 4.4 Hz, 1H), 2.80 (dt, J = 7.5 Hz, 4.8 Hz, 1H), 2.47 (dd, J = 14.5 Hz, 6.8 Hz, 1H), 2.33 (ABX, J = 14.8 Hz, 4.5 Hz, 1H), 2.27 (ABX, J = 14.8 Hz, 7.2 Hz, 1H), 2.10 (dd, J = 14.7 Hz, 4.5 Hz), 1.60 (s, 3H), 1.49 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 207.4 (C), 165.2 (C), 161.4 (C), 130.9 (C), 127.2 (C), 125.9 (C), 124.8 (CH), 115.1 (CH), 108.4 (CH), 55.5 (CH_3), 47.3 (CH), 38.5 (CH), 35.5 (CH_2), 31.5 (CH_2), 19.4 (CH_3), 19.1 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ (M^+): 242.1307 Found: 242.1309. The ortho isomer eluted second, and was isolated as a yellow wax in 18% yield. **(4aR*,9aS*)-1,4,4a,9a-Tetrahydro-8-methoxy-2,3-dimethylfluoren-9-one (7g):** ^1H NMR (CDCl_3 , 500 MHz) δ 7.49 (t, J = 7.8 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 3.89 (s, 3H), 3.50 (dt, J = 7.3 Hz, 4.7 Hz, 1H), 2.78 (dt, J = 7.5 Hz, 4.5 Hz, 1H), 2.46 (dd, J = 14.7 Hz, 6.8 Hz, 1H), 2.36 (ABX, J = 14.8 Hz, 4.3 Hz, 1H), 2.26 (ABX, J = 14.8 Hz, 7.2 Hz, 1H), 2.10 (dd, J = 14.6 Hz, 4.3 Hz), 1.61 (s, 3H), 1.47 (s, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 207.0 (C), 161.4 (C), 157.4 (C), 136.3 (CH), 127.3 (C), 125.8 (C), 125.7 (CH), 117.0 (CH), 108.7 (CH), 55.7 (CH_3), 47.4 (CH), 38.1 (CH), 35.6 (CH_2), 31.6 (CH_2), 19.4 (CH_3), 19.2 (CH_3); HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ (M^+): 242.1307 Found: 242.1309.

Synthesis of Benztetrahydrofluorenones 7h-7k:

General Procedure B: A flame-dried round bottom flask equipped with a condenser under N_2 with an outlet for SO_2 was charged with Meldrum's acid alkylidene (200 mg, 1.0

equiv). Sultine **5d**¹³ (1.1 equiv) was weighed into a vial, and rinsed into the flask with (CH₂Cl)₂ (0.2 M relative to the alkylidene). The contents were heated to reflux for 16 hours and cooled to rt before removing a 50 μ L aliquot to check the reaction progress by ¹H NMR. A solution of BF₃•OEt₂ (CH₂Cl)₂ in (0.1 equiv/100 μ L) was added to the flask, as well as enough (CH₂Cl)₂ to bring the total volume to 0.15 M. The reaction was heated to reflux for the indicated times and then cooled to rt. The remainder of the procedure is identical to A.

Meldrum's Acid 4a + Sultine 5d: The FC acylation was heated to reflux for 3.5 hours. Isolated as a white powder in 87% yield after flash chromatography eluting with 1:4 EtOAc:hexanes. **(4bS*,10aR*)-1,3-Dimethoxy-5,10,10a,11-tetrahydro-4bH-benzo[b]-fluoren-11-one (7h):** M.p. 183-185 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.14-7.01 (m, 4H), 6.55 (s, 1H), 6.20 (d, *J*= 1.3Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.60 (q, *J*= 6.7 Hz, 1H), 3.15 (dd, *J*= 14.3 Hz, 6.5 Hz, 1H), 3.05-2.84 (m, 3H), 2.73 (dd, *J*= 14.3 Hz, 6.6 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.0 (C), 167.2 (C), 162.8 (C), 159.1 (C), 137.2 (C), 136.8 (C), 127.6 (CH), 127.2 (CH), 126.6 (CH), 126.3 (CH), 119.6 (C), 100.6 (CH), 97.4 (CH), 55.68 (CH₃), 55.66 (CH₃), 47.6 (CH), 38.7 (CH), 34.4 (CH₂), 30.6 (CH₂); HRMS(EI) *m/z* calcd for C₁₉H₁₈O₃ (M⁺): 294.1256 Found: 294.1255.

Meldrum's Acid 4e + Sultine 5d: 2.0 equiv of diene was used instead of 1.1 equiv and the FC acylation was run for 6.5 hours. Isolated as a white powder in 52% yield after flash chromatography eluting with 1:9 EtOAc:hexanes. **(4bS*,10aR*)-3,4-Dimethoxy-5,10,10a,11-tetrahydro-4bH-benzo[b]fluoren-11-one (7i):** M.p. 133-135 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.40 (d, *J*= 8.4 Hz, 1H), 7.16-7.06 (m, 4H), 6.91 (d, *J*= 8.4 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 3.83 (q, *J*= 7.0 Hz, 1H), 3.27 (dd, *J*= 14.3 Hz, 6.5 Hz, 1H), 3.10-2.84 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ 206.7 (C), 158.1 (C), 149.9 (C), 145.8 (C), 137.5 (C), 137.0 (C), 131.2 (C), 127.45 (CH), 127.35 (CH), 126.5 (CH), 126.4 (CH), 120.1 (CH), 112.7 (CH), 60.5 (CH₃), 56.1 (CH₃), 47.5 (CH), 37.2 (CH), 32.9 (CH₂), 30.5 (CH₂); HRMS(EI) *m/z* calcd for C₁₉H₁₈O₃ (M⁺): 294.1256 Found: 294.1256.

Meldrum's Acid 4f + Sultine 5d: The FC acylation was heated to reflux for 4 hours. Isolated as a white powder in 74% yield after flash chromatography eluting with 1:4 EtOAc:hexanes. **(4bS*,10aR*)-2-Bromo-1,3-dimethoxy-5,10,10a,11-tetrahydro-4bH-benzo[b]fluoren-11-one (7j):** M.p. 181-182 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.13-6.99 (m, 4H), 6.77 (s, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 3.67 (q, *J*= 6.6 Hz, 1H), 3.19 (dd, *J*= 14.3 Hz, 6.5 Hz, 1H), 3.09-2.90 (m, 3H), 2.76 (dd, *J*= 14.3 Hz, 6.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 202.9 (C), 162.4 (C), 160.6 (C), 156.1 (C), 136.8 (C), 136.4 (C), 127.6 (CH), 127.3 (CH), 126.8 (CH), 126.6 (CH), 123.5 (C), 106.6 (CH), 102.8 (CH), 61.9 (CH₃), 56.8 (CH₃), 47.7 (CH), 38.9 (CH), 34.5 (CH₂), 30.8 (CH₂); HRMS(EI) *m/z* calcd for C₁₉H₁₇BrO₃ (M⁺): 372.0361 Found: 372.0355.

Meldrum's Acid 4g + Sultine 5d: The FC acylation was heated to reflux for 5.5 hours. Isolated as a white powder in 71% yield by flash chromatography eluting with 1:9 EtOAc:hexanes. **(6bS*,12aR*)-7,12,12a,13-tetrahydro-6bH-dibenzo[a,h]fluoren-13-one (7k):** M.p. 155-156 °C; ¹H NMR (CDCl₃, 300 MHz) δ 9.08 (d, *J*= 8.3 Hz, 1H), 8.05 (d, *J*= 8.4 Hz, 1H), 7.84 (d, *J*= 8.1 Hz, 1H), 7.62 (d, *J*= 8.2 Hz, 1H), 7.59 (d, *J*= 1.0 Hz, 1H), 7.53-7.48 (m, 1H), 7.17 (d, *J*= 6.8 Hz, 1H), 7.10-7.01 (m, 3H), 3.86 (q, *J*= 6.6 Hz, 1H), 3.29 (dd, *J*= 14.4 Hz, 6.6 Hz, 1H), 3.21-3.02 (m, 3H), 2.89 (dd, *J*= 14.4 Hz, 6.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 208.6 (C), 160.5 (C), 136.9 (C), 136.7 (C), 136.2 (CH), 131.4 (C), 129.0 (C), 129.0 (CH), 128.9 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 126.7 (CH), 126.6 (CH), 126.5 (CH), 124.2 (CH), 122.5 (CH), 47.5 (CH), 39.0 (CH), 34.1 (CH₂), 30.8 (CH₂); HRMS(EI) *m/z* calcd for C₂₁H₁₆O (M⁺): 284.1201 Found: 284.1203.

Preparation of Arylbutadienes 5g and 5h:

(*E*)-1-aryl-1,3-butadienes were prepared from the appropriate benzaldehyde and diethylallylphosphonate according to the procedure of Wang and West.¹⁴ They were stored in a fridge in the dark for up to two weeks.

5-((*E*)-Buta-1,3-dienyl)-1,3-dimethoxybenzene (5g): Prepared from 3,5-dimethoxybenzaldehyde and isolated as a clear, colourless oil in 33% yield. ¹H NMR (CDCl₃, 300 MHz) δ 6.75 (dd, *J*= 10.5 Hz, 15.5 Hz, 1H), 6.55 (brs, 2H), 6.51 (brs, 1H), 6.45-6.35 (m, 2H), 5.33 (d, *J*= 16.8 Hz, 1H), 5.17 (d, *J*= 9.7 Hz, 1H), 3.79 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 160.9 (C), 139.1 (C), 137.0 (CH), 132.8 (CH), 130.1 (CH), 117.9 (CH), 104.4 (CH), 100.0 (CH), 55.3 (CH₃); HRMS(EI) *m/z* calcd for C₁₂H₁₄O₂ (M⁺): 190.0994 Found: 190.1000.

4-((*E*)-Buta-1,3-dienyl)-1,2-dimethoxybenzene (5h)¹⁵: Prepared from 3,4-dimethoxybenzaldehyde and isolated as a clear, colourless oil in 23% yield. ¹H NMR (CDCl₃, 300 MHz) δ 6.94 (s, 1H), 6.93 (overlapping d, 1H, *J*= 8.2 Hz, 1H), 6.80 (d, *J*= 8.0 Hz, 1H), 6.66 (dd, *J*= 15.5 Hz, 10.2 Hz, 1H), 6.53-6.40 (m, 2H), 5.28 (d, *J*= 16.9 Hz, 1H), 5.11 (d, *J*= 9.8 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 149.0 (C), 148.8 (C), 137.2 (CH), 132.6 (CH), 130.1 (C), 127.8 (CH), 119.8 (CH), 116.6 (CH₂), 111.0 (CH), 108.5 (CH), 55.8 (CH₃), 55.7 (CH₃); HRMS(EI) *m/z* calcd for C₁₂H₁₄O₂ (M⁺): 190.0994 Found: 190.0987.

Synthesis of DA adducts 6e-6i and tetrahydrofluorenones 7o-7s:

General Procedure C: The reactions were performed and worked up according to General Procedure A. Separation of the two products was achieved by flash chromatography eluting with 1:9 EtOAc:hexanes to elute the unreacted endo DA adduct. The polarity of

the mobile phase was increased to 1:4 EtOAc:hexanes and elution continued to isolate the fluorenone product.

Arylbutadiene 5g + Meldrum's acid 4h: The DA reaction gave an exo:endo ratio of 66:34. After treatment with $\text{BF}_3 \cdot \text{OEt}_2$, the endo adduct **6e** was isolated as a white powder in 20% yield. M.p. 145-146 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.31-7.22 (m, 5H), 6.38 (d, $J = 2.2$ Hz, 2H), 6.33 (t, $J = 2.2$ Hz, 1H), 6.17-6.12 (m, 1H), 5.83 (dd, $J = 10.3$ Hz, 1.7 Hz, 1H), 4.48 (brs, 1H), 3.79 (dd, $J = 11.7$ Hz, 5.5 Hz, 2H), 3.72 (s, 6H), 3.09-3.00 (m, 1H), 2.46 (dt, $J = 18.3$ Hz, 5.2 Hz), 0.71 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.6 (C), 163.9 (C), 160.9 (C), 141.1 (C), 138.8 (C), 128.9 (CH), 128.8 (CH), 128.0 (CH), 127.9 (CH), 126.3 (CH), 107.2 (CH), 105.5 (C), 100.6 (CH), 59.9 (C), 55.4 (CH₃), 50.3 (CH), 47.7 (CH), 29.1 (CH₂), 28.7 (CH₃), 28.2 (CH₃); HRMS(EI) m/z calcd for $\text{C}_{25}\text{H}_{26}\text{O}_6$ (M^+): 422.1729 Found: 422.1734. The fluorenone was isolated as a yellow oil in 58% yield. **(1S*,4aS*,9aR*)-1,2-Dihydro-6,8-dimethoxy-1-phenyl-4aH-fluoren-9(9aH)-one (7o):** ^1H NMR (CDCl_3 , 300 MHz) δ 7.35-7.16 (m, 5H), 6.52 (d, $J = 1.4$ Hz, 1H), 6.30 (d, $J = 1.7$ Hz, 1H), 5.94 (br d, $J = 10.0$ Hz, 1H), 5.81-5.74 (m, 1H), 3.88-3.87 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.62 (dd, $J = 9.5$ Hz, 4.0 Hz), 3.09-3.00 (dd, $J = 6.1$ Hz, 4.3 Hz, 1H), 2.34 (doublet of sextet, $J = 17.6$ Hz, 2.8 Hz, 1H), 2.21 (br d, $J = 17.7$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 201.8 (C), 167.0 (C), 161.0 (C), 159.4 (C), 145.2 (C), 128.3 (CH), 127.8 (CH), 127.7 (CH), 126.4 (CH), 126.0 (CH), 117.0 (C), 100.9 (CH), 97.6 (CH), 55.8 (CH₃), 55.7 (CH₃), 53.4 (CH), 38.7 (CH), 37.7 (CH), 28.3 (CH₂); HRMS(EI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3$ (M^+): 320.1412 Found: 320.1410.

Arylbutadiene 5g + Meldrum's Acid 4i : The DA reaction gave an exo:endo ratio of 69:31. After treatment with $\text{BF}_3 \cdot \text{OEt}_2$, the endo adduct **6f** was isolated as a white powder in 24% yield after eluting with 3:17 EtOAc:hexanes. M.p. 147-149 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.14 (d, $J = 8.7$ Hz, 1H), 6.81 (d, $J = 8.7$ Hz, 2H), 6.37 (d, $J = 2.2$ Hz, 2H), 6.32 (t, $J = 2.2$ Hz, 1H), 6.15-6.10 (m, 1H), 5.81 (dd, $J = 10.2$ Hz, 1.8 Hz, 1H), 4.46 (br s, 1H), 3.77-3.72 (m, 1H), 3.74 (s, 3H), 3.72 (s, 6H), 3.03-2.94 (m, 1H), 2.42 (dt, $J = 18.4$ Hz, 5.2 Hz, 1H), 0.71 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.8 (C), 164.1 (C), 161.0 (C), 159.4 (C), 141.2 (C), 130.9 (C), 130.0 (CH), 128.1 (CH), 126.3

(CH), 114.1 (CH), 107.2 (CH), 105.5 (C), 100.6 (CH), 60.1 (C), 55.4 (CH₃), 55.2 (CH₃), 50.4 (CH), 47.0 (CH), 29.4 (CH₂), 28.8 (CH₃), 28.5 (CH₃); HRMS(EI) m/z calcd for C₂₆H₂₈O₇ (M⁺): 452.1835 Found: 452.1845. The fluorenone was isolated as a yellow oil in 53% yield, after eluting with 1:2 EtOAc:hexanes. **(1S*,4aS*,9aR*)-1,2-Dihydro-6,8-dimethoxy-1-(4-methoxyphenyl)-4aH-fluoren-9(9aH)-one (7p)**: ¹H NMR (CDCl₃, 300 MHz) δ 7.24 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 1.1 Hz, 1H), 6.29 (d, J = 1.7 Hz, 1H), 5.94 (br d, J = 9.9 Hz 1H), 5.81-5.75 (m, 1H), 3.88-3.80 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H), 3.53 (dd, J = 9.6 Hz, 4.5 Hz, 1H), 3.04 (dd, J = 6.3 Hz, 4.7 Hz, 1H), 2.34-2.28 (m, 1H), 2.24 (br d, J = 18.0 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.9 (C), 167.0 (C), 161.0 (C), 159.4 (C), 157.8 (C), 137.2 (C), 128.6 (CH), 127.6 (CH), 126.6 (CH), 117.1 (C), 113.6 (CH), 100.9 (CH), 97.5 (CH), 55.8 (CH₃), 55.7 (CH₃), 55.2 (CH₃), 53.6 (CH), 38.7 (CH), 37.1 (CH), 28.7 (CH₂); HRMS(EI) m/z calcd for C₂₂H₂₂O₄ (M⁺): 350.1518 Found: 350.1519.

Arylbutadiene 5g + Meldrum's acid 4j: The DA reaction gave an exo:endo ratio of 65:35. After treatment with BF₃•OEt₂, the endo adduct **6g** was isolated as a white powder in 23% yield. M.P. 204-206 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.24-7.21 (m, 3H), 7.13-7.09 (m, 1H), 6.36 (d, J = 2.2 Hz, 2H), 6.33 (t, J = 2.2 Hz, 1H), 6.15-6.08 (m, 1H), 5.82 (dd, J = 10.3 Hz, 1.9 Hz, 1H), 4.49 (br s, 1H), 3.78-3.72 (m, 1H), 3.72 (s, 6H), 3.03-2.92 (m, 1H), 2.44 (dt, J = 18.3 Hz, 5.2 Hz), 0.75 (s, 3H), 0.71 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.3 (C), 163.7 (C), 161.0 (C), 140.9 (C), 140.8 (C), 134.7 (C), 130.1 (CH), 128.8 (CH), 128.3 (CH), 127.6 (CH), 127.2 (CH), 126.3 (CH), 107.2 (CH), 105.6 (C), 100.6 (CH), 59.5 (C), 55.4 (CH₃), 50.4 (CH), 47.5 (CH), 29.2 (CH₂), 28.7 (CH₃), 28.4 (CH₃); HRMS(EI) m/z calcd for C₂₅H₂₅ClO₆ (M⁺): 456.1340 Found: 456.1340. The fluorenone was isolated as a yellow oil in 55% yield. **(1S*,4aS*,9aR*)-1-(3-Chlorophenyl)-1,2-dihydro-6,8-dimethoxy-4aH-fluoren-9(9aH)-one (7q)**: ¹H NMR (CDCl₃, 300 MHz) δ 7.31 (s, 1H), 7.22-7.14 (m, 3H), 6.52 (d, J = 1.4 Hz, 2H), 6.30 (d, J = 1.8 Hz, 1H), 5.96 (br d, J = 10.0 Hz 1H), 5.80-5.73 (m, 1H), 3.88-3.84 (br s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.56 (dd, J = 9.7 Hz, 4.1 Hz, 1H), 3.04 (dd, J = 6.6 Hz, 4.4 Hz, 1H), 2.31 (doublet of sextet, J = 17.6 Hz, 3.0 Hz), 2.20 (br d, J = 17.7 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.2 (C), 167.1 (C), 160.7 (C), 159.4 (C), 147.2 (C), 133.9 (C),

129.4 (CH), 127.8 (CH), 127.7 (CH), 126.1 (CH), 126.0 (CH), 116.7 (C), 100.9 (CH), 97.5 (CH), 55.7 (CH₃), 53.0 (CH), 38.4 (CH), 37.6 (CH), 28.1 (CH₂); HRMS(EI) m/z calcd for C₂₁H₁₉ClO₃ (M⁺): 354.1023 Found: 354.1021.

Arylbutadiene 5g + Meldrum's acid 4k: The DA reaction gave an exo:endo ratio of 64:36. After treatment with BF₃•OEt₂, the endo adduct **6h** was isolated as a white powder in 24% yield. M.P. 161-163 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.26 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 6.36 (d, J = 2.2 Hz, 2H), 6.33 (t, J = 2.2 Hz, 1H), 6.15-6.08 (m, 1H), 5.82 (dd, J = 10.3 Hz, 2.0 Hz, 1H), 4.54 (brs, 1H), 3.79-3.72 (m, 1H), 3.72 (s, 6H), 3.09-2.91 (m, 1H), 2.42 (dt, J = 18.4 Hz, 5.3 Hz) 0.74 (s, 3H), 0.70 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.4 (C), 163.8 (C), 140.9 (C), 137.3 (C), 134.0 (C), 130.3 (CH), 128.9 (CH), 127.7 (CH), 126.4 (CH), 107.2 (CH), 105.6 (C), 100.6 (CH), 59.7 (C), 55.4 (CH₃), 50.3 (CH), 47.3 (CH), 29.2 (CH₂), 28.7 (CH₃), 28.5 (CH₃); HRMS(EI) m/z calcd for C₂₅H₂₅ClO₆ (M⁺): 456.1340 Found: 456.1338. The fluorenone was isolated as a yellow oil in 51% yield. **(1S*,4aS*,9aR*)-1-(4-Chlorophenyl)-1,2-dihydro-6,8-dimethoxy-4aH-fluoren-9(9aH)-one (7r):** ¹H NMR (CDCl₃, 300 MHz) δ 7.24 (s, 4H), 6.51 (d, J = 1.4 Hz, 1H), 6.29 (d, J = 1.8 Hz, 1H), 5.96 (br d, J = 10.0 Hz 1H), 5.80-5.75 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.82-3.81 (m, 1H), 3.50 (dd, J = 9.9 Hz, 4.7 Hz, 1H), 3.04 (dd, J = 6.2 Hz, 5.5 Hz, 1H), 2.29 (doublet of sextet, J = 17.4 Hz, 2.9 Hz, 1H), 2.19 (br d, J = 17.5 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.4 (C), 167.1 (C), 160.8 (C), 159.4 (C), 143.5 (C), 131.7 (C), 129.0 (CH), 128.3 (CH), 127.7 (CH), 126.2 (CH), 116.8 (C), 100.9 (CH), 97.5 (CH), 55.7 (CH₃), 53.2 (CH), 38.5 (CH), 37.5 (CH), 28.5 (CH₂); HRMS(EI) m/z calcd for C₂₁H₁₉ClO₃ (M⁺): 354.1023 Found: 354.1023.

Arylbutadiene 5h + Meldrum's acid 4h: The DA reaction gave an exo:endo ratio of 65:35 After treatment with BF₃•OEt₂, the endo adduct **6i** was isolated as a white powder in 21% yield. M.P. 160-162 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.30-7.21 (m, 5H), 7.13-7.09 (m, 1H), 6.76 (s, 2H), 6.73 (s, 1H), 6.17-6.11 (m, 1H), 5.82 (dd, J = 10.2 Hz, 2.0 Hz, 1H), 4.49 (br s, 1H), 3.83-3.76 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.09-2.97 (m, 1H), 2.46 (dt, J = 18.3 Hz, 5.2 Hz), 0.65 (s, 3H), 0.60 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.8 (C), 164.1 (C), 149.1 (C), 148.7 (C), 138.9 (C), 131.3 (C), 128.92 (CH), 128.87

(CH), 128.8 (CH), 128.1 (CH), 127.9 (CH), 126.7 (CH), 121.8 (C), 112.3 (CH), 111.1 (C), 105.5 (CH), 60.3 (C), 55.9 (CH₃), 49.9 (CH), 47.6 (CH), 29.1 (CH₂), 28.9 (CH₃), 28.2 (CH₃); HRMS(EI) *m/z* calcd for C₂₅H₂₆O₆ (M⁺): 422.1729 Found: 422.1721.

Using the solvent system described in General Procedure C, the fluorenone product was isolated with 10-15% contamination with the endo adduct **6i**. This was further purified by flash chromatography using 1:19 acetone:toluene to yield the fluorenone as a yellow oil in 45% yield. **(1S*,4aS*,9aR*)-1,2-dihydro-6,7-dimethoxy-1-phenyl-4aH-fluoren-9(9aH)-one (7s)**: ¹H NMR (CDCl₃, 300 MHz) δ 7.32-7.20 (m, 5H), 7.17 (s, 1H), 6.92 (s, 1H), 6.05 (dd, *J*= 10.0 Hz, 1.8 Hz, 1H), 5.84-5.79 (m, 1H), 3.97-3.89 (br s, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 3.44 (dd, *J*= 10.6 Hz, 5.3 Hz, 1H), 3.12 (t, *J*= 6.0 Hz, 1H), 2.27 (t, *J*= 4.4 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.7 (C), 155.6 (C), 151.3 (C), 149.6 (C), 144.8 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 126.5 (CH), 126.3 (CH), 106.3 (CH), 104.7 (CH), 56.3 (CH₃), 56.1 (CH₃), 53.2 (CH), 39.0 (CH), 38.7 (CH), 29.2 (CH₂); HRMS(EI) *m/z* calcd for C₂₁H₂₀O₃ (M⁺): 320.1412 Found: 320.1410.

Synthesis of Tetrahydrofluorenones **7t-7u**:

General Procedure D: An oven-dried Schlenk tube cooled under N₂ was charged with 5-(1-methylethylidene) Meldrum's acid **4l**¹⁶ (100 mg, 0.54 mmol, 1.0 equiv). The arylbutadiene (X equiv) was weighed into a vial, then transferred into the tube with (CH₂Cl)₂ (0.4 M). The tube was sealed and heated to 100 °C for 16 hours, then cooled to rt. A 50 μL aliquot was removed to check conversion by ¹H NMR, then a solution of BF₃•OEt₂ in (CH₂Cl)₂ (0.1 equiv/100 μL) was washed into the tube with sufficient (CH₂Cl)₂ to bring the concentration to 0.15 M. The reaction was reheated to 100 °C for 30 minutes, cooled to rt., and worked up as in Procedure A. Flash chromatography eluting with 1:9 to 1:4 EtOAc:hexanes afforded a yellow powder, which was recrystallized from Et₂O to remove coloured impurities.

Arylbutadiene 5h + Meldrum's Acid 4l: Prepared by General Procedure D using 2.2 equiv of diene **5h**; the DA reaction proceeded to 89% completion and the product was isolated as a white powder in 81% yield. **(4aR*,9aR*)-1,2-Dihydro-6,7-dimethoxy-1,1-dimethyl-4aH-fluoren-9(9aH)-one (7t):** M.p. 138-140 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.11 (s, 1H), 6.91 (s, 1H), 6.02 (br d, *J*= 9.9 Hz, 1H), 5.78-5.71 (m, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 3.78 (br s, 1H), 2.61 (d, *J*= 6.7 Hz, 1H), 1.93 (ABX, *J*= 16.9 Hz, 2.6 Hz, 1H), 1.84 (ABX, *J*= 16.9 Hz, 4.9 Hz, 1H) 1.24 (s, 3H), 0.80 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 206.0 (C), 155.3 (C), 150.4 (C), 149.3 (C), 129.5 (C), 126.4 (CH), 125.9 (CH), 105.5 (CH), 104.0 (CH), 56.2 (CH₃), 56.0 (CH₃), 39.2 (CH), 38.8 (CH₂), 32.5 (C), 29.1 (CH₃), 24.1 (CH₃); HRMS(EI) *m/z* calcd for C₁₇H₂₀O₃ (M⁺): 272.1412 Found: 272.1404.

Arylbutadiene 5g + Meldrum's Acid 4l: Prepared by General Procedure D using 3.0 equiv of diene **5g**. The DA reaction proceeded to 79% completion and the product was isolated as a white solid in 26% yield. **(4aR*,9aR*)-1,2-Dihydro-6,8-dimethoxy-1,1-dimethyl-4aH-fluoren-9(9aH)-one (7u):** M.p. 164-166 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.55 (s, 1H), 6.31 (s, 1H), 6.00 (br d, *J*= 10.0 Hz, 1H), 5.79-5.75 (m, 1H), 3.913 (s, 3H), 3.908 (s, 3H), 3.76 (br s, 1H), 2.61 (d, *J*= 7.0 Hz, 1H), 1.93 (app t, *J*= 1.8 Hz, 2H), 1.25 (s, 3H), 0.90 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 203.3 (C), 166.8 (C), 160.3 (C), 159.1 (C), 126.7 (CH), 125.7 (CH), 118.8 (C), 99.9 (CH), 97.3 (CH), 56.6 (CH₃), 55.73 (CH₃), 55.70 (CH₃), 39.5 (CH), 38.6 (CH₂), 32.4 (C), 29.0 (CH₃), 24.3 (CH₃); HRMS(EI) *m/z* calcd for C₁₇H₂₀O₃ (M⁺): 272.1412 Found: 272.1407.

References:

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Spectral Data:

5-[(3,5-dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4a):

5-[(3,4-dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4b):

27.418

55.941
56.147

76.574
76.998
77.422

104.104
110.497
110.587
115.589

125.033
132.594

148.676
154.672
158.165
160.565
164.065

AD-3-267-1
13C
June 18/06

ppm

5-[(3,4,5-trimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4c):

AD-3-34-1
13C
June 18/05

5-[(3-methoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4d):

5-[(2,3-dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4e):

5-[(4-bromo-3,5-dimethoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione

(4f):

5-[(4-methoxyphenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4i):

AD-40ME
¹³C
 July 14/06

27.457

55.638

76.574
 76.998
 77.422

104.109

110.824

114.326

124.707

137.587

157.852

160.418

163.991

164.604

ppm

5-[(3-chlorophenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4j):

27.628

77.425
77.001
76.577

104.784

116.235

129.835
131.321
132.496
133.126
133.197
134.634

155.994
159.307
162.681

AD-3-126-1
13C
June 22/06

ppm

5-[(4-chlorophenyl)methylene]-2,2-dimethyl-1,3-dioxane-4,6-dione (4k):

Adduct 6a: Meldrum's acid 4a + butadiene sulphone 5a

27.905
28.775
29.764
34.753

46.265
52.586
55.278

76.574
76.999
77.422

100.176
104.871
106.679

120.988
127.018

141.531

160.836
166.940
170.746

AD-2-153-1
13C
July 13/06

ppm

Adduct 6b: Meldrum's acid 4a + 2,3-dimethylbutadiene 5b

18.268
 18.971
 28.015
 29.809
 35.038
 40.782
 47.003
 53.943
 55.354
 76.577
 77.000
 77.201
 77.424

100.187
 104.789
 106.667

119.802
 126.152

141.732

160.870
 167.038
 171.080

AD-2-165-1
 C13
 July 13/06

ppm

Endo adduct 6c: Meldrum's acid 5a + 1-((*E*)-buta-1,3-dienyl)benzene 5e

28.494
28.564
29.398

47.762
50.682
55.328
59.815

76.580
77.003
77.427

100.356
105.509
106.819

126.316
127.982
128.019
128.806
129.512
138.843
141.214

160.938
163.869
169.535

SH-1-174-A
13C
July 19/06

ppm

Exo adduct 6c: Meldrum's acid 5a + 1-((*E*)-buta-1,3-dienyl)benzene 5e

(4b*R,8a*S**)-4b,5,8,8a-tetrahydro-1,3-dimethoxyfluoren-9-one (7a):**

24.543
28.502

37.596

46.811

55.628
55.661

76.421
76.997
76.573

97.301
100.461

119.615
126.945
128.517

158.802
163.678
167.051

204.705

ppm

AD-3-132-1
13C
June 26/06

(4a*R,9a*S**)-1,4,4a,9a-tetrahydro-6,8-dimethoxy-2,3-dimethylfluoren-9-one (7b):**

AD-2-272-1
13C
June 28/06

19.080	19.343
31.514	35.476
38.289	47.505
55.582	55.618
76.744	76.999
77.254	
97.158	100.304
119.886	127.268
126.628	158.635
163.621	166.844
204.947

(4a*R,9a*S**)-1,4,4a,9a-tetrahydro-6,8-dimethoxy-3-methylfluoren-9-one (7c):**

(4aR*,9aS*)-1,4,4a,9a-tetrahydro-6,7-dimethoxy-2,3-dimethylfluoren-9-one (7d):

AD-2-281-1
Flashed 20%
July 1/06

AD-2-281-1
13C
July 1/06

(4a*R,9a*S**)-1,4,4a,9a-tetrahydro-6,7,8-trimethoxy-2,3-dimethylfluoren-9-one**

(7e):

(4a*R,9a*S**)-1,4,4a,9a-tetrahydro-6-methoxy-2,3-dimethylfluoren-9-one (7f):**

19.386
19.114

31.512
35.535
38.459

47.305

55.538

76.742
76.996
77.251

108.447

115.069

124.796
125.896
127.195
130.913

161.425

165.322

207.355

ppm

AD-3-135-1
C-13
June 28/06

(4a*R,9a*S**)-1,4,4a,9a-tetrahydro-8-methoxy-2,3-dimethylfluoren-9-one**

(7g):

19.395
19.193

31.556
35.609
36.072

47.368

55.692

75.745
77.000
77.254

108.677

117.036

125.746
125.833
127.290

136.318

157.365

161.358

205.994

ppm

AD-3-135-2
13C
June 28/06

(4b*S,10a*R**)-1,3-dimethoxy-5,10,10a,11-tetrahydro-4b*H*-benzo[*b*]fluoren-11-one**

(7h):

AD-3-63-1
13C
July 11/06

(4b*S,10a*R**)-3,4-dimethoxy-5,10,10a,11-tetrahydro-4b*H*-benzo[*b*]fluoren-11-one**

(7i):

AD-3-141-1
C13
July 11/06

(4b*S,10a*R**)-2-bromo-1,3-dimethoxy-5,10,10a,11-tetrahydro-4b*H*-benzo[*b*]fluoren-11-one (7j):**

AD-3-71-1
Flashed 20%
May 9/06

AD-3-71-1
¹³C, 1H decouple
 May 16/05

(6b*S**,12a*R**)-7,12,12a,13-tetrahydro-6*bH*-dibenzo[*a,h*]fluoren-13-one

(7k):

AD-3-88-1
Flashed 10%
July 13/06

47.521
38.993
34.074
30.760

77.423
77.000
76.576

160.508
136.896
136.653
136.180
132.637
131.362
129.044
128.901
127.991
127.527
127.342
126.701
126.622
126.500
124.213
122.507

208.619
ppm

AD-3-88-1
C13
July 13/06

(1*R,4*aR**,9*aR**)-1,4,4*a*,9*a*-tetrahydro-6,8-dimethoxy-1-phenylfluoren-9-one**

(7l):

29.358
36.494
39.964

54.851
55.608

76.572
76.997
77.421

97.375
100.605

118.068
125.946
126.281
127.696
128.357
130.868

144.464

159.010
163.387
166.958

202.415

ppm

AD-3-149-1
13C
July 19/05

Alkylidene Meldrum's Acid 4a + 5f: Endo Adduct 6d

AD-3-129-1
13C
July 8/06

(1*R,4*aR**,9*aS**)-1,4,4*a*,9*a*-tetrahydro-6,8-dimethoxy-1-methylfluoren-9-one (7m):**

AD-3-129-2
Flashed 15-20%
July 9/06

37.652
30.514
28.864
20.532

55.696
55.655
54.226

77.426
77.002
76.578

100.495
97.407

135.115
125.481
118.803

166.955
163.361
159.115

203.985

ppm

AD-3-129-2
13C
July 9/06

(1*S,4*aR**,9*aS**)-1,4,4*a*,9*a*-tetrahydro-6,8-dimethoxy-1-methylfluoren-9-one (7n):**

5-((*E*)-buta-1,3-dienyl)-1,3-dimethoxybenzene (5g)

AD-3-143-1
C13
July 14/06

160.852
139.064
136.951
132.779
130.061
117.943
104.411
99.998
77.422
76.998
76.575
55.274

ppm

4-((*E*)-buta-1,3-dienyl)-1,2-dimethoxybenzene (5h)

Endo adduct 6e

29.090
28.741
28.208

59.876
55.359
50.308
47.718

77.427
77.003
76.579

107.185
105.483
100.558

141.084
138.760
128.887
128.795
128.085
127.922
126.238

169.564
163.896
160.931

AD-3-144-1
C13
July 15/06

ppm

(1S*,4aS*,9aR*)-1,2-dihydro-6,8-dimethoxy-1-phenyl-4aH-fluoren-9(9aH)-one

(7o):

Endo adduct 6f

(1*S,4*aS**,9*aR**)-1,2-dihydro-6,8-dimethoxy-1-(4-methoxyphenyl)-4*aH*-fluoren-9(9*aH*)-one (7p):**

Endo adduct 6g

29.165
28.658
28.382

59.524
55.353
50.365
47.516

77.425
77.001
76.577

107.181
105.603
100.621

140.907
140.812
134.655
130.041
128.846
128.290
127.626
127.194
126.311

169.281
163.705
160.974

AD-3-147-1
13C
July 17/06

ppm

(1*S,4*aS**,9*aR**)-1-(3-chlorophenyl)-1,2-dihydro-6,8-dimethoxy-4*aH*-fluoren-
9(9*aH*)-one (7q):**

Endo adduct 6h

AD-3-145-1
Flashed 10%
July 17/06

29.192
28.697
28.508

59.720
55.387
50.263
47.291

77.424
77.001
76.577

107.243
105.601
100.572

140.922
137.288
133.998
130.266
128.908
127.665
126.357

169.426
163.814
161.009

AD-3-146-1
13C
July 17/06

ppm

(1*S**,4*aS**,9*aR**)-1-(4-chlorophenyl)-1,2-dihydro-6,8-dimethoxy-4*aH*-fluoren-
9(9*aH*)-one (7r):

Endo adduct 6i

AD-3-111-2
Flashed 15%
July 4/06

29.072
28.869
28.183

60.292
55.889
49.911
47.593

77.426
77.002
76.578

149.079
148.699
138.852
131.349
128.872
128.826
128.093
127.872
126.672
121.798
112.341
111.121
105.488

169.771
164.104

AD-3-111-2
13C
July 6/06

ppm

(1S*,4aS*,9aR*)-1,2-dihydro-6,7-dimethoxy-1-phenyl-4aH-fluoren-9(9aH)-one

(7s):

(4aR*,9aR*)-1,2-dihydro-6,7-dimethoxy-1,1-dimethyl-4aH-fluoren-9(9aH)-one (7t):

AD-3-117-1
13C
June 22/05

(4aR*,9aR*)-1,2-dihydro-6,8-dimethoxy-1,1-dimethyl-4aH-fluoren-9(9aH)-one (7u):

AD-3-145-1
13C
July 17/06

ORTEP diagram of endo 6c:

Ellipsoids are drawn to the 30% probability level