Supporting Information 1

Experimental Section

Meldrum's Acids as Acylating Agents in the Catalytic Intramolecular Friedel-Crafts Reaction

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General Methods. All reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. Nitromethane and DMF were distilled from CaH_2 . $\text{Sc}(\text{OTf})_3$ was dried under high vacuum (0.5 mmHg) for 2 hours at 180 °C and stored in a dry-box. ^1H NMR spectra were referenced to residual ^1H shift in CDCl_3 (7.24 ppm). CDCl_3 (77.0 ppm) was used as the internal reference for ^{13}C NMR spectra. Reactions were monitored by thin-layer chromatography (TLC) on commercial silica pre-coated plates with a particle size of 60 Å. Developed plates were viewed by UV lamp (254 nm), and with *p*-anisaldehyde stain. Flash chromatography was performed using 230-400 mesh silica gel. Melting points are uncorrected. Methyl¹, and dimethyl Meldrum's alkylidenes² were prepared according to literature procedures. Cyclohexyl, tetrahydro-4-pyran, tetrahydro-4-thiopyran, and 4-cyclohexanone (ethylene ketal) Meldrum's alkylidenes were prepared from their respective ketones according to the method of Baty.³

General Procedure A - Preparation of Mono-Benzyl Meldrum's Acids via a One-Pot Reductive Alkylation: Meldrum's acid (1 eq) and the appropriate benzaldehyde (0.98 eq) were dissolved in absolute EtOH (0.5-1.0 M), followed by the addition of catalytic piperidinium acetate (0.1 eq). The resulting solution was stirred vigorously for 30 minutes, and then cooled to 0 °C. NaBH_3CN (1.5 eq) was added portion-wise over 60 minutes, and the reaction allowed to warm to room temperature. The reaction was monitored by TLC and upon completion was carefully quenched with 10% HCl (*extreme caution should be exercised due to the evolution of HCN gas*). Vigorous stirring was maintained until gas evolution had ceased, after which time the reaction was concentrated in vacuo to remove EtOH. The residue was re-suspended in 10% HCl and extracted four times with CH_2Cl_2 . The combined organic layers were

dried over MgSO_4 , filtered, and concentrated. The resulting product was generally found to be of good purity by ^1H NMR, but was recrystallized from MeOH or purified by flash chromatography on silica gel.

General Procedure B - Alkylation of 5-Substituted Meldrum's Acid and Dialkylation of Meldrum's Acid: Equivalents are doubled for the dialkylation. Anhydrous K_2CO_3 (1.5 eq) was added to a solution of 5-substituted Meldrum's acid (1 eq) in dry DMF (1.0 M). To the vigorously stirred suspension was added dropwise the appropriate electrophile, such as iodomethane (5-10 eq), allyl bromide (1.2 eq), propargyl bromide (1.2 eq), or benzyl bromides (1.1 eq). The reaction was monitored by TLC (typical reaction times are 30-120 minutes for activated electrophiles and 16-24 hours for iodomethane). Upon completion, the mixture was poured into water (15 vol eq relative to DMF) and extracted 3 times with EtOAc. The combined organic layers were washed twice with saturated aqueous NaHCO_3 , brine, dried over MgSO_4 , filtered and concentrated. The resulting crude products were typically very pure by ^1H NMR and nearly quantitative in yield, but were purified by recrystallization or flash chromatography on silica gel.

General Procedure C - Conjugate Addition of Grignard Reagents to Meldrum's Alkylidenes: In a typical reaction, Meldrum's alkylidene was suspended in dry THF (0.1 M) and cooled to $0\text{ }^\circ\text{C}$ with stirring under inert atmosphere. A solution of the appropriate Grignard reagent (2 eq) in THF (or Et_2O) (0.5 to 3 M) was added dropwise over one hour, and then the reaction allowed to warm to room temperature and monitored by TLC. Upon completion, the reaction was quenched with 5% HCl and extracted three times with EtOAc. The combined organic layers were washed with H_2O , brine, then dried over MgSO_4 and filtered. Concentrated provided the crude product that was purified by either recrystallization or by flash chromatography on silica gel.

General Procedure D - Intramolecular Metal Trifluoromethanesulfonate – Catalyzed Friedel-Crafts Acylation of Meldrum's Acid Derivatives: Reactions were typically performed on 200 milligrams of substrate. In a flame-dried round bottomed flask equipped with a magnetic stir bar, a reflux condenser and under inert atmosphere, was placed the substrate and $\text{Sc}(\text{OTf})_3$ (0.1 eq) (or other solid catalyst; liquid catalysts were administered to a solution of the substrate in CH_3NO_2). Distilled CH_3NO_2 was added in one portion by syringe, and the resulting suspension immediately placed into an oil bath preheated to $100\text{ }^\circ\text{C}$. The reaction was maintained at this temperature and monitored by TLC until complete consumption of starting material was observed. The reaction was then concentrated under vacuum and directly subjected to flash chromatography, using a small quantity of CH_2Cl_2 to assist column loading.

The slow (syringe pump) addition of a substrate solution to a stirring suspension of $\text{Sc}(\text{OTf})_3$ at 100 °C was found to be advantageous for less activated π -nucleophiles.

5,6-Dimethoxy-1-indanone⁴ (2): Prepared from **27** in 59% yield using Procedure D in 45 min. Purified by flash chromatography (6:5 hexanes:EtOAc) to provide a white solid. M.p. 116-118 °C (CH_2Cl_2). Lit. 119.5-120.5 °C and 118.8-119.5 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.13 (s, 1H), 6.85 (s, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.03-2.99 (m, 2H), 2.65-2.61 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.7, 155.3, 150.4, 149.3, 129.8, 107.4, 104.1, 56.1, 56.0, 36.4, 25.5; HRMS m/z calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$ (M^+): 192.0786. Found: 192.0787.

Dimethyl 2-(3,5-dimethoxybenzyl)-2-methylmalonate (4): Compound **(3)** was alkylated according to Procedure B using iodomethane. Recrystallization from MeOH provided white crystals in 70% yield. M.p. 75-76 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.28 (s, 1H), 6.20 (s, 2H), 3.69-3.68 (br s, 12H), 3.12 (s, 2H), 1.31 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 172.1, 160.4, 138.0, 108.1, 98.6, 55.0, 54.6, 52.3, 41.3, 19.6; HRMS(EI) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_6$ (M^+): 296.1260. Found: 296.1249.

5-(3,5-Dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (9): Prepared by reductive alkylation of Meldrum's acid with 3,5-dimethoxybenzaldehyde using Procedure A. Recrystallization from MeOH provided a fine white solid in 61% yield. M.p. 102-103 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.44 (d, $J = 2.3$ Hz, 2H), 6.29 (app t, $J = 2.2$ Hz, 1H), 3.73 (t, $J = 4.9$ Hz, 1H), 3.37 (d, $J = 4.9$ Hz, 2H), 1.70 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.2, 160.7, 139.6, 107.4, 105.1, 99.1, 55.2, 47.9, 32.1, 28.4, 27.0; Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}_6$: C, 61.22; H, 6.16. Found: C, 61.28; H, 6.26.

5,7-Dimethoxy-1-indanone⁵ (10): Prepared from **9** in 73% yield using Procedure D in 60 min. Purified by flash chromatography using 2:1 EtOAc:hexanes; M.p. 98-99 °C (benzene/petroleum ether). Lit. 98-99 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 6.42 (br s, 1H), 6.24 (br s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.98-2.94 (m, 2H), 2.60-2.56 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 203.3, 166.8, 160.3, 159.2, 119.3, 101.5, 97.3, 55.6, 36.8, 25.8. Anal. calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.74; H, 6.29. Found: C, 69.03; H, 6.30.

5-[1-(3,5-Dimethoxyphenyl)ethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (11): Prepared by conjugate addition of 3,5-dimethoxyphenylmagnesium chloride to methyl Meldrum's alkylidene using Procedure C in 49% yield after recrystallization from MeOH. M.p. 111-112 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.53-6.52 (m, 2H), 6.36-6.31 (m, 1H), 3.95 (dq, $J = 7.2, 2.9$ Hz, 1H), 3.78 (s, 6H), 3.69 (d, $J = 3.0$ Hz, 1H), 1.69 (s, 3H), 1.64 (d, $J = 7.3$ Hz, 3H), 1.40 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz)

δ 164.9, 164.8, 160.8, 143.5, 106.4, 105.2, 99.4, 55.3, 52.4, 39.7, 28.2, 27.9, 17.8; Anal. calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.05; H, 6.61.

5,7-Dimethoxy-3-methyl-1-indanone (12): Prepared from **11** in 77% yield using Procedure D in 60 min. Purified by flash chromatography using 2:1 EtOAc:hexanes; M.p. 61-62.5 °C; 1H NMR ($CDCl_3$, 300 MHz) δ 6.45 (br s, 1H), 6.27 (br s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.28-3.22 (m, 1H), 2.85 (dd, J = 18.5, 7.6 Hz, 1H), 2.21 (dd, J = 18.5, 3.5 Hz, 1H), 1.32 (d, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.4, 167.0, 165.2, 159.0, 118.6, 100.4, 97.2, 55.7, 55.6, 45.9, 32.5, 21.3. Anal. calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.82; H, 6.73.

5-[1-(3,5-Dimethoxyphenyl)-1-methylethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (13): Prepared by conjugate addition of 3,5-dimethoxyphenylmagnesium chloride to dimethyl Meldrum's alkylidene using Procedure C to provide a 76% yield of white solid after recrystallization from MeOH. M.p. 121-122 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.46-6.45 (m, 2H), 6.33-6.31 (m, 1H), 3.75 (s, 6H), 3.59 (s, 1H), 1.63 (s, 3H), 1.61 (s, 6H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.0, 160.6, 147.4, 105.0, 104.8, 98.1, 57.1, 55.2, 42.5, 28.9, 27.6, 27.5; Anal. Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88. Found: C, 63.22; H, 7.06.

5,7-Dimethoxy-3,3-dimethyl-1-indanone⁶ (14): Prepared from **13** in 82% yield using Procedure D with CH_3CN in 120 min. Purified by flash chromatography using 2:1 EtOAc:hexanes; M.p. 92-94 °C (Et₂O). Lit. 95.5 °C (benzene); 1H NMR ($CDCl_3$, 300 MHz) δ 6.44 (br s, 1H), 6.27 (br s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.52 (s, 2H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.6, 168.9, 167.0, 158.8, 117.5, 98.8, 96.9, 55.7, 55.6, 53.4, 37.9, 29.7. Anal. calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.87; H, 7.49.

5-[1-(3,5-Dimethoxyphenyl)cyclohexyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (15): Prepared by conjugate addition of 3,5-dimethoxyphenylmagnesium chloride to cyclohexyl Meldrum's alkylidene using Procedure C to provide a 78% yield of white solid after recrystallization from MeOH. M.p. 124-125 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.38 (m, 2H), 6.29 (m, 1H), 3.60 (s, 6H), 3.38 (s, 1H), 2.38-2.33 (m, 2H), 2.00-1.90 (m, 2H), 1.70-1.50 (m, 2H), 1.44 (s, 3H), 1.44-1.30 (m, 4H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 160.9, 142.1, 105.9, 105.4, 99.0, 56.6, 55.2, 47.2, 35.6, 30.3, 26.4, 25.4, 22.3; Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.36; H, 7.33.

5,7-Dimethoxy-(3.3)-pentamethylene-1-indanone (16): Prepared from **15** in 83% yield using Procedure D with CH₃CN in 120 min. Purified by flash chromatography using 1:1 EtOAc:hexanes; M.p. 132-133 °C (Et₂O); ¹H NMR (CDCl₃, 300 MHz) δ 6.45 (d, *J* = 1.8 Hz, 1H), 6.26 (d, *J* = 1.8 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.51 (s, 2H), 1.76-1.19 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.9, 169.3, 166.9, 159.0, 117.8, 99.3, 97.2, 55.8, 55.7, 49.1, 42.7, 38.2, 25.4, 23.6. Anal. calcd for C₁₆H₂₀O₃: C, 73.82; H, 7.74. Found: C, 73.93; H, 7.83.

5-[4-(3,5-Dimethoxyphenyl)tetrahydro-2H-4-pyranyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (17): Conjugate addition of 3,5-dimethoxyphenylmagnesium chloride to tetrahydro-4-pyran Meldrum's alkydine using Procedure C provided a clear, colorless solid after recrystallization from MeOH in 73% yield. M.p. 147-148 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.34 (s, 3H), 3.84-3.77 (m, 2H), 3.71 (s, 6H), 3.60-3.47 (m, 2H), 2.50-2.45 (m, 2H), 2.30-2.22 (m, 2H), 1.48 (s, 3H), 0.86 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.9, 161.3, 140.9, 105.8, 105.7, 99.4, 64.0, 55.6, 55.3, 45.3, 36.0, 30.2, 26.7; Anal. Calcd C₁₅H₁₈O₆: C, 62.63; H, 6.64. Found: C, 62.53; H, 6.71.

5,7-Dimethoxy-[3.3]-(3',4',6',7')tetrahydropyran-1-indanone (18): Prepared from **17** in 79% yield using Procedure D with Yb(OTf)₃ in 15 min. Purified by flash chromatography (3:1 EtOAc:hexanes) to provide a white solid. M.p. 201-203 °C (EtOAc/hexanes); ¹H NMR (CDCl₃, 300 MHz) δ 6.47 (s, 1H), 6.28 (s, 1H), 3.96 (dd, *J* = 11.8, 4.4 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.48 (br t, *J* = 12.3 Hz, 2H), 2.58 (s, 2H), 2.06 (dt, *J* = 13.1, 4.6 Hz, 2H), 1.36 (br d, *J* = 13.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 200.4, 167.2, 167.1, 159.1, 117.8, 99.3, 97.5, 65.4, 55.8, 55.7, 48.4, 40.2, 38.0; HRMS(EI) *m/z* calcd for C₁₅H₁₈O₄ (M⁺): 262.1205. Found: 262.1209.

5-[4-(3,5-Dimethoxyphenyl)tetrahydro-2H-4-thiopyranyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (19): Conjugate addition of 3,5-dimethoxy phenylmagnesium chloride to tetrahydro-4-thiopyranyl Meldrum's alkydine according to Procedure C produced a 69% yield of the desired product as a white powder after recrystallization from MeOH. M.p. 135-136 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.33 (s, 3H), 3.71 (s, 6H), 3.41 (s, 1H), 2.85-2.55 (m, 6H), 2.50-2.30 (m, 2H), 1.47 (s, 3H), 0.89 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 163.8, 161.2, 140.5, 106.0, 105.7, 99.2, 56.4, 55.3, 46.3, 36.5, 30.3, 26.5, 24.1; HRMS(EI) *m/z* calcd for C₁₉H₂₄O₆S (M⁺): 380.1293. Found: 380.1302.

5,7-Dimethoxy-[3.3]-(3',4',6',7')tetrahydrothiopyran-1-indanone (20): Prepared from **19** in 86% yield using Procedure D with Yb(OTf)₃ in 20 min. Purified by flash chromatography (1:1 hexanes:EtOAc)

to provide a white solid. M.p. 196-197 °C (CH₂Cl₂); ¹H NMR (CDCl₃, 300 MHz) δ 6.49 (d, *J* = 1.8 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.84-2.74 (m, 2H), 2.59-2.54 (m, 2H), 2.49 (s, 2H), 2.10-2.00 (m, 2H), 1.79-1.72 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 200.4, 167.9, 167.1, 159.2, 117.5, 99.3, 97.7, 55.8, 47.9, 41.7, 38.4, 25.7; HRMS(EI) *m/z* calcd for C₁₅H₁₈O₃S (M⁺): 278.0977. Found: 278.0974.

5-[8-(3,5-Dimethoxyphenyl)-1,4-dioxaspiro[4.5]dec-8-yl]-2,2-dimethyl-1,3-dioxane-4,6-dione (21): Conjugate addition of 3,5-dimethoxyphenylmagnesium chloride to cyclohexyl-4-one (ethylene ketal) Meldrum's alkylidene using Procedure C produced a 78% yield following recrystallization from MeOH. M.p. 139-140 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.25-6.23 (m, 3H), 3.82-3.77 (m, 4H), 3.63 (s, 6H), 3.33 (s, 1H), 2.50-2.40 (m, 2H), 2.20-2.00 (m, 2H), 1.70-1.40 (m, 4H), 1.40 (s, 3H), 0.78 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.0, 160.9, 140.6, 107.6, 105.8, 105.4, 99.1, 64.0, 55.7, 55.1, 46.0, 32.7, 31.1, 30.0, 26.4; HRMS(EI) *m/z* calcd for C₂₂H₂₈O₈ (M⁺): 420.1784. Found: 420.1783.

5,7-Dimethoxy-[3.3]cyclohexan-6'-one (ethylene ketal)-1-indanone (22): Prepared from **21** in 78% yield using Procedure D with powdered 5Å molecular sieves (1 eq) and Yb(OTf)₃ in 21 hours. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a pale yellow solid. M.p. 152-154 °C (CH₂Cl₂); ¹H NMR (CDCl₃, 300 MHz) δ 6.51 (d, *J* = 1.6 Hz, 1H), 6.29 (d, *J* = 1.6 Hz, 1H), 3.98 (d, *J* = 1.7 Hz, 4H), 3.88 (d, *J* = 1.8 Hz, 3H), 3.86 (d, *J* = 1.6 Hz, 3H), 2.57 (d, *J* = 1.8 Hz, 2H), 2.09-2.05 (m, 2H), 1.82-1.61 (m, 4H), 1.56-1.51 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.1, 168.1, 167.1, 159.1, 118.0, 108.0, 99.1, 97.8, 64.4, 64.3, 55.8, 48.3, 41.8, 35.8, 32.6; HRMS(EI) *m/z* calcd for C₁₈H₂₂O₅ (M⁺): 318.1467. Found: 318.1463.

5-(3,5-Dimethylbenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (23): Reductive alkylation of Meldrum's acid according to Procedure A with 3,5-dimethylbenzaldehyde provided a clear colorless oil after flash chromatography (62 %) which solidified on standing. M.p. 69-70 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.91 (br s, 2H), 6.85 (br s, 1H), 3.72 (t, *J* = 4.9 Hz, 1H), 3.39 (d, *J* = 4.9 Hz, 2H), 2.60 (s, 6H), 1.72 (s, 3H), 1.48 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.4, 138.1, 137.2, 128.7, 127.3, 105.2, 48.2, 31.9, 28.4, 27.1, 21.2; HRMS(EI) *m/z* calcd for C₁₅H₁₈O₄ (M⁺): 262.1205. Found: 262.1206.

5,7-Dimethyl-1-indanone⁷ (24): Prepared from **23** in 52% yield following Procedure D using the slow addition of substrate over 9.5 h. Purified by flash chromatography using 8:1 hexanes:EtOAc; M.p. 75-76 °C (MeOH). Lit. 76-77 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.05 (s, 1H), 6.89 (s, 1H), 3.02-2.98 (m,

2H), 2.64-2.60 (m, 2H), 2.57 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.5, 156.5, 145.0, 138.5, 132.2, 130.3, 124.4, 36.1, 25.2, 21.8, 18.2. Anal. calcd for $\text{C}_{11}\text{H}_{12}\text{O}$: C, 82.46; H, 7.55. Found: C, 82.40; H, 7.36.

5-[1-(3,5-Dimethylphenyl)cyclohexyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (25): Prepared by conjugate addition of 3,5-dimethylphenylmagnesium bromide to cyclohexyl Meldrum's alkylidene according to Procedure C, and recrystallized using MeOH to provide a white solid in 88% yield. M.p. 144.5-146 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.87 (br s, 3H), 3.42 (s, 1H), 2.46-2.41 (m, 2H), 2.26 (s, 6H), 2.04-1.96 (m, 2H), 2.75-2.60 (m, 2H), 1.46 (s, 3H), 1.46-1.40 (m, 4H), 0.71 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.2, 139.5, 137.8, 128.6, 125.1, 105.4, 56.5, 46.7, 38.4, 30.3, 25.8, 25.5, 22.1, 21.2; Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4$: C, 72.70; H, 7.93. Found: C, 72.65; H, 7.89.

5,7-Dimethyl-(3.3)-pentamethylene-1-indanone (26): Prepared from **25** in 75% yield using Procedure D in 90 min. Purified by flash chromatography using 10:1 hexanes:EtOAc; M.p. 87.5-88.5 °C (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.08 (s, 1H), 6.89 (s, 1H), 2.57 (s, 3H), 2.52 (s, 2H), 2.37 (s, 3H), 1.77-1.23 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 206.5, 165.6, 145.0, 138.2, 130.5, 121.7, 49.1, 42.1, 38.4, 25.6, 23.8, 22.0, 18.3. Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83. Found: C, 84.00; H, 9.12.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione⁸ (27): Prepared by reductive alkylation of Meldrum's acid with 3,4-dimethoxybenzaldehyde according to Procedure A. A fine white powder was obtained in 77% yield after recrystallization from MeOH. M.p. 136-137 °C (MeOH). Lit. 142-144 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 6.77-6.64 (m, 3H), 3.75-3.73 (br s, 7H), 3.32 (d, J = 4.8 Hz, 2H), 1.63 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.3, 148.4, 147.7, 129.3, 121.7, 112.8, 110.8, 104.9, 55.5, 47.9, 31.5, 28.1, 26.9; HRMS(EI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{O}_6$ (M^+): 294.1103. Found: 294.1106.

5-[1-(3,4-Dimethoxyphenyl)ethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (28): Conjugate addition of methylmagnesium iodide to 3,4-dimethoxyphenyl Meldrum's alkylidene (prepared by condensation of 3,4-dimethoxybenzaldehyde with Meldrum's acid)⁹ according to Procedure C produced a 53% yield of a white powder after recrystallization from MeOH. M.p. 137-138 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.82-6.79 (m, 2H), 6.72-6.69 (m, 1H), 3.87 (dq, J = 7.3, 3.0 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.63 (d, J = 3.0 Hz, 1H), 1.59 (s, 6H), 1.26 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.2, 164.7, 148.5, 148.0, 133.3, 120.3, 111.4, 110.7, 105.0, 55.6, 55.3, 39.2, 27.9, 27.7, 18.2; HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_6$ (M^+): 308.1260. Found: 308.1269.

5,6-Dimethoxy-3-methyl-1-indanone⁴ (29): Prepared from **28** in 68% yield using Procedure D in 20 min. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a white solid. M.p. 87-88 °C (hexanes/EtOAc). Lit. 90.5-92 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.12 (s, 1H), 6.86 (s, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.36-3.30 (m, 1H), 2.92 (dd, *J* = 7.2, 1.2 Hz, 1H), 2.23 (dd, *J* = 18.8, 1.4 Hz, 1H), 1.35 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.7, 155.4, 155.2, 149.3, 129.1, 106.0, 103.8, 56.1, 56.0, 45.4, 32.4, 21.3; HRMS(EI) *m/z* calcd for C₁₂H₁₄O₃ (M⁺): 206.0943. Found: 206.0949.

5-[1-(3,4-Dimethoxyphenyl)-1-methylethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (30): Conjugate addition of 3,4-dimethoxyphenylmagnesium bromide to dimethyl Meldrum's alkylidene according to Procedure C provided a white solid in 49% yield after recrystallization from EtOH. M.p. 137-138 °C (EtOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.86-6.75 (m, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.46 (s, 1H), 1.63 (s, 6H), 1.56 (s, 3H), 1.19 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 148.5, 148.0, 136.5, 118.7, 110.7, 110.1, 105.2, 57.7, 55.9, 55.8, 42.7, 29.5, 28.2, 27.2; Anal. Calcd for C₁₇H₂₂O₆: C, 63.34; H, 6.88. Found: C, 63.69; H, 6.93.

5,6-Dimethoxy-3,3-dimethyl-1-indanone⁴ (31): Prepared from **30** in 69% yield using Procedure D in 20 min. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.14 (s, 1H), 6.87 (s, 1H), 4.01 (s, 3H), 3.92 (s, 3H), 2.58 (s, 2H), 1.42 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.4, 159.2, 155.6, 149.4, 128.1, 104.3, 103.8, 56.2, 56.1, 52.9, 38.2, 29.9; HRMS(EI) *m/z* calcd for C₁₃H₁₆O₃ (M⁺): 220.1099. Found: 220.1108.

5-(2,5-Dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (32): Prepared by the reductive alkylation of Meldrum's acid with 2,5-dimethoxybenzaldehyde according to Procedure A, and recrystallized from MeOH to give a yield of 57%. M.p. 94-95 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.91 (s, 1H), 6.74 (d, *J* = 2.2 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.34 (d, *J* = 5.8 Hz, 2H), 1.75 (s, 3H), 1.70 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.3, 153.3, 151.3, 126.7, 117.8, 112.5, 104.8, 60.4, 55.7, 46.1, 28.6, 28.0, 26.4; HRMS(EI) *m/z* calcd for C₁₅H₁₈O₆ (M⁺): 294.1103. Found: 294.1095.

4,7-Dimethoxy-1-indanone¹⁰ (33): Prepared from **32** in 32% yield using Procedure D in 20 min. Purified by flash chromatography (1:1 hexanes:EtOAc) to provide a white solid. M.p. 122-123 °C (Et₂O). Lit. 125-126 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.96 (d, *J* = 8.7 Hz, 1H), 6.70 (d, *J* = 8.7 Hz, 1H), 3.88 (s, 3H), 2.96 (AB m, 2H), 2.65 (AB m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.3, 151.8, 150.4, 145.9, 126.3, 116.5, 109.4, 55.9, 36.7, 22.2; HRMS(EI) *m/z* for C₁₇H₁₇NO₃ (M⁺): 192.0786. Found: 192.0782.

5-(2-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-5-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-

dione (34): Obtained by reductive alkylation of Meldrum's acid with TBDPS-protected 4-methoxysalicylaldehyde according to Procedure A. Flash chromatography (10:3 hexanes:EtOAc), followed by recrystallization from MeOH gave a white solid in 21% yield. M.p. 128-129 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.71-6.80 (m, 4H), 7.46-7.35 (m, 6H), 7.01 (br s, 1H), 6.38-6.36 (m, 2H), 4.49 (t, *J* = 6.0 Hz, 1H), 3.69 (s, 3H), 3.54 (d, *J* = 6.0 Hz, 2H), 1.73 (s, 3H), 1.62 (s, 3H), 1.10 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.9, 153.3, 147.0, 135.1, 132.5, 130.0, 128.1, 127.9, 118.9, 117.7, 112.4, 124.8, 55.4, 46.7, 48.6, 27.7, 26.5, 25.6, 19.3; HRMS(EI) *m/z* calcd for C₃₀H₃₄O₆Si (M⁺): 518.2125. Found: 518.2142.

4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-7-methoxy-1-indanone (35): Prepared from **34** in 63% yield using Procedure D in 35 min. Purified by flash chromatography (3:1 hexanes:EtOAc) to provide a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.72 (dd, *J* = 7.9, 1.4 Hz, 4H), 7.42-7.31 (m, 6H), 6.64 (d, *J* = 6.6 Hz, 1H), 6.41 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H), 3.11 (t, *J* = 5.8 Hz, 2H), 2.70 (t, *J* = 5.9 Hz, 1H), 1.15 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.0, 152.1, 147.3, 146.1, 135.4, 132.5, 130.1, 127.9, 126.1, 125.0, 109.4, 55.8, 36.8, 26.5, 22.8, 19.5; HRMS(EI) *m/z* calcd for C₂₆H₂₈O₃Si (M⁺): 416.1808. Found: 416.1799.

5-(2,3-Dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (36): Prepared by the reductive alkylation of Meldrum's acid with veratraldehyde according to Procedure A. Recrystallization from MeOH provided white crystals in 44% yield. M.p. 120-121 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.00-6.95 (m, 2H), 6.80 (dd, *J* = 7.5, 2.1 Hz, 1H), 4.11 (t, *J* = 5.6 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.34 (d, *J* = 5.6 Hz, 2H), 1.75 (s, 3H), 1.71 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.2, 152.4, 146.9, 131.8, 123.9, 123.4, 111.2, 104.9, 60.4, 55.6, 47.1, 29.6, 27.4, 26.2; Anal. Calcd for C₁₅H₁₈O₆: C, 61.22; H, 6.16. Found: C, 61.26; H, 6.17; HRMS(EI) *m/z* calcd for C₁₅H₁₈O₆ (M⁺): 294.1103. Found: 294.1109.

4,5-Dimethoxy-1-indanone¹¹ (37): Prepared from **36** in 64% yield using Procedure D in 80 min. Purified by flash chromatography (1:1 hexanes:EtOAc) to provide a pale yellow solid. M.p. 68-70 °C (Et₂O). Lit. 74 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.46 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.07-3.02 (AB m, 2H), 2.63-2.59 (AB m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.4, 157.4, 147.8, 145.9, 131.0, 120.1, 112.2, 60.2, 56.1, 36.3, 22.4; HRMS(EI) *m/z* calcd for C₁₁H₁₂O₃ (M⁺): 192.0786. Found: 192.0782.

5-[1-(2,3-Dimethoxyphenyl)ethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (38): The target material was obtained by the conjugate addition of Me_2AlCl to 2,3-dimethoxyphenyl Meldrum's alkylidene (prepared by condensing 2,3-dimethoxybenzaldehyde with Meldrum's acid)⁹. A white powder was obtained in 51% yield after flash chromatography (3:1 hexanes:EtOAc) and recrystallization from MeOH. M.p. 123-123.5 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.08–7.03 (m, 2H), 6.86-6.82 (m, 1H), 4.29 (d, J = 2.9 Hz, 1H), 4.12 (dq, J = 7.1, 2.9 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H), 1.43 (d, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.5, 163.5, 152.1, 146.3, 135.6, 123.7, 120.9, 110.9, 104.6, 60.6, 55.6, 50.8, 31.6, 28.3, 26.7, 13.9; HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{O}_6$ (M^+): 308.1260. Found: 308.1251.

4,5-Dimethoxy-3-methyl-1-indanone (39): Prepared from **38** in 38% yield using Procedure D in 40 min. Purified by flash chromatography (3:1 hexanes:EtOAc) to provide a clear colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.45 (d, J = 8.4 Hz), 6.93 (d, J = 8.4 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 3.51 (ddq, J = 7.7, 7.0, 2.6 Hz, 1H), 2.87 (dd, J = 18.9, 7.7 Hz, 1H), 2.22 (dd, J = 18.9, 2.6 Hz, 1H), 1.38 (d, 7.0 Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.0, 158.0, 152.3, 145.8, 130.6, 119.9, 112.4, 60.5, 56.1, 45.8, 30.8, 21.0; HRMS(EI) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$ (M^+): 206.0943. Found: 206.0937.

5-[1-(2,3-Dimethoxyphenyl)-1-methylethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (40): Conjugate addition of 2,3-dimethoxyphenylmagnesium bromide to dimethyl Meldrum's alkylidene according to Procedure C provided a 25% yield of white solid after flash chromatography (6:1 hexanes:EtOAc). M.p. 118-119 °C (CH_2Cl_2); ^1H NMR (CDCl_3 , 300 MHz) δ 7.02-6.94 (m, 2H), 6.81 (dd, J = 7.2, 2.3 Hz, 1H), 5.38 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 1.77 (s, 3H), 1.65 (s, 3H), 1.63 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 163.6, 152.3, 146.4, 140.2, 123.1, 118.7, 110.7, 103.6, 60.4, 55.3, 53.5, 39.5, 28.4, 25.9, 25.5; HRMS(EI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_6$ (M^+): 322.1416. Found: 322.1419.

5-(2-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-3-methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (42): Reductive alkylation of Meldrum's acid with TBDPS-protected *o*-vanillin according to Procedure A, followed by flash chromatography (8:1 hexanes:EtOAc) gave a 32% yield of white solid. M.p. 116-118 °C (Benzene); ^1H NMR (CDCl_3 , 300 MHz) δ 7.63 (dd, J = 7.6, 1.8 Hz, 4H), 7.38-7.28 (m, 6H), 6.98 (dd, J = 7.7, 1.3 Hz, 1H), 6.81 (app t, J = 7.9 Hz, 1H), 6.49 (dd, J = 8.1, 1.4 Hz, 1H), 4.33 (t, J = 6.2 Hz, 1H), 3.57 (d, J = 6.2 Hz, 2H), 2.76 (s, 1H), 1.72 (s, 3H), 1.61 (s, 3H), 1.02 (s, 9H); ^{13}C NMR

(CDCl₃, 75 MHz) δ 165.0, 148.7, 142.8, 135.3, 134.0, 129.0, 127.2, 123.7, 120.8, 110.3, 104.5, 53.3, 46.7, 28.8, 27.9, 26.8, 25.7, 20.0; HRMS(EI) m/z calcd for C₃₀H₃₄O₆Si (M⁺-CH₃): 503.1890. Found: 503.1905.

4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-5-methoxy-1-indanone (43): Prepared from **42** in 50% yield using Procedure D in 40 min. Purified by flash chromatography (10:1 hexanes:EtOAc) to provide a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.66 (d, J = 7.1 Hz, 4H), 7.37-7.29 (m, 4H), 6.65 (d, J = 8.3 Hz, 1H), 3.11-3.07 (m, 2H), 3.09 (s, 3H), 2.66-2.63 (AB m, 2H), 1.09 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.8, 154.5, 145.7, 141.5, 134.7, 134.1, 131.1, 129.4, 127.3, 117.6, 111.6, 54.4, 36.5, 26.7, 23.2, 20.0; HRMS(EI) m/z calcd for C₂₆H₂₈O₃Si (M⁺-CH₃): 401.1573. Found: 401.1581.

5-3-Methoxy-2-[(1,1,1-triisopropylsilyl)oxy]benzyl-2,2-dimethyl-1,3-dioxane-4,6-dione (44): Reductive alkylation of Meldrum's acid with TIPS-protected *o*-vanillin according to Procedure A, followed by flash chromatography (6:1 hexanes:EtOAc) and recrystallization from MeOH gave a 21% yield of white solid. M.p. 77-78 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.96 (dd, J = 7.5, 1.3 Hz, 1H), 6.83 (app t, J = 7.8 Hz, 1H), 6.74 (dd, J = 8.1, 1.4 Hz, 1H), 4.15 (t, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.39 (d, J = 6.0 Hz, 2H), 1.79 (s, 3H), 1.76 (s, 3H), 1.28 (septet, J = 7.7 Hz, 3H), 1.10 (d, J = 7.3 Hz, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.0, 149.3, 143.5, 128.3, 124.1, 120.3, 109.1, 104.7, 54.5, 46.6, 28.7, 27.7, 25.9, 18.0, 14.2; HRMS(EI) m/z calcd for C₂₃H₃₆O₆Si (M⁺-CH₃): 421.2046. Found: 421.2056.

5-Methoxy-4-[(1,1,1-triisopropylsilyl)oxy]-1-indanone (45): Prepared from **44** in 45% yield using Procedure D in 40 min. Purified by flash chromatography (12:1 hexanes:EtOAc) to provide a pale yellow solid. M.p. 59-60 °C (Et₂O); ¹H NMR (CDCl₃, 300 MHz) δ 7.36 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.04 (t, J = 5.9 Hz, 2H), 2.64 (dd, J = 6.1, 4.8 Hz, 2H), 1.24 (septet, J = 7.9 Hz, 3H), 1.07 (d, J = 7.1 Hz, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 206.0, 154.9, 146.1, 142.2, 131.2, 117.1, 111.4, 55.3, 36.5, 23.1, 18.0, 13.7; HRMS(EI) m/z calcd for C₁₉H₃₀O₃Si (M⁺): 334.1964. Found: 334.1966.

2,2-Dimethyl-5-(1-phenylcyclohexyl)-1,3-dioxane-4,6-dione (48): Conjugate addition of phenylmagnesium bromide to cyclohexyl Meldrum's alkylidene according to Procedure C provided a 66% yield of product following recrystallization from hexanes. M.p. 106-107 °C (hexanes); ¹H NMR (CDCl₃, 300 MHz) δ 7.35-7.22 (m, 5H), 3.44 (s, 1H), 2.5-2.45 (m, 2H), 2.05-1.97 (m, 2H), 1.66-1.61 (m, 2H), 1.45 (s, 3H), 1.45-1.32 (m, 4H), 0.71 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 139.6, 128.7, 127.7, 127.3, 105.7, 57.2, 47.2, 35.5, 30.6, 26.2, 25.7, 22.3; Anal. Calcd for C₁₈H₂₂O₄: C, 71.50; H, 7.33. Found: C, 71.40; H, 7.32.

(3.3)-Pentamethylene-1-indanone¹² (49): Prepared from **48** in 56% yield using Procedure D in 30 min. Purified by flash chromatography using 7:1 hexanes:EtOAc to provide a colorless oil. Lit. M.p. 58-59 °C (petroleum ether); ¹H NMR (CDCl₃, 300 MHz) δ 7.65 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 2.53 (s, 3H), 1.75-1.20 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.9, 164.0, 135.4, 134.7, 127.4, 123.8, 123.3, 48.2, 43.0, 38.2, 25.3, 23.7. Anal. calcd for C₁₄H₁₆O: C, 83.96; H, 8.05. Found: C, 83.60; H, 8.12.

5-(5-Chloro-1-methyl-1-phenylpentyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (50): Meldrum's acid and 6-chloro-2-hexanone were condensed according to the procedure of Brown¹³, to provide the chlorobutyl methyl Meldrum's alkylidene in quantitative yield and was used without further purification. Subsequent conjugate addition according to Procedure C using phenylmagnesium bromide produced the desired compound in 51% yield as an oil following flash chromatography (5:1 hexanes:EtOAc). M.p. 84-85 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.34-7.20 (m, 5H), 3.60 (s, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.14-2.06 (m, 2H), 1.77-1.68 (m, 2H), 1.64 (s, 3H), 1.59 (s, 3H), 1.42-1.37 (m, 1H), 1.18 (s, 3H), 1.18-1.08 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 163.9, 142.3, 128.5, 127.1, 126.6, 105.2, 57.2, 45.8, 44.6, 39.3, 32.8, 29.3, 27.2, 22.3, 21.7; HRMS(EI) *m/z* calcd for C₁₈H₂₃ClO₄ (M⁺): 338.1285. Found: 338.1292.

3-(4-Chlorobutyl)-3-methyl-1-indanone (51): Prepared from **50** in 52% yield using Procedure D in 15 min. Purified by flash chromatography (8:1 hexanes:EtOAc) to provide a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.54 (AB quartet, *J* = 18.9 Hz, 2H), 1.76-1.60 (m, 4H), 1.50-1.39 (m, 1H), 1.39 (s, 3H), 1.1-0.95 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.8, 162.4, 135.9, 134.9, 127.5, 123.7, 123.3, 50.0, 44.5, 41.9, 41.3, 32.9, 28.3, 22.3; HRMS(EI) *m/z* calcd for C₁₄H₁₇ClO (M⁺): 236.0968. Found: 236.0971.

5-(3-Methoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (52): Prepared by reductive alkylation of Meldrum's acid with *m*-anisaldehyde using Procedure A in 45 % yield after recrystallization from MeOH. M.p. 102-104 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.15 (app t, *J* = 8.0 Hz, 1H), 6.86-6.84 (m, 2H), 6.75-6.72 (m, 1H), 3.77 (t, *J* = 5.0 Hz, 1H), 3.73 (s, 3H), 3.40 (d, *J* = 5.0 Hz, 2H), 1.69 (s, 3H), 1.49 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.2, 159.4, 138.7, 129.4, 121.7, 115.1, 112.5, 105.1, 55.0, 47.8, 31.8, 28.2, 26.8; Anal. Calcd for C₁₄H₁₆O₅: C, 63.63; H, 6.10. Found: C, 63.70; H, 6.15.

5-Methoxy-1-indanone (53) and 7-Methoxy-1-indanone (54): Prepared from **52** in 52% yield as a 5.5:1 ratio of para **53**:ortho **54** products using Procedure D in 60 min. The mixture was separated with 2:1 hexanes:EtOAc; (**53**): M.p. 108-109 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.68-7.65 (m, 1H), 6.89-6.87 (m, 2H), 3.86 (s, 3H), 3.07 (m, 2H), 2.65 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.3, 165.2, 158.2, 130.4, 125.3, 115.3, 109.7, 55.6, 36.4, 25.8. Anal. calcd for C₁₀H₁₀O₂: C, 74.06; H, 6.21. Found: C, 73.90; H, 6.27. (**54**): M.p. 96-97.5 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.50 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 3.08-3.04 (m, 2H), 2.68-2.63 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.9, 158.1, 158.0, 136.4, 125.2, 118.4, 108.8, 55.7, 36.8, 25.5. HRMS(EI): *m/z* calcd for C₁₀H₁₀O₂ (M⁺): 162.0681. Found 162.0685.

5-[1-(3-Methoxyphenyl)cyclohexyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (55): Conjugate addition of 3-methoxyphenylmagnesium bromide to cyclohexyl Meldrum's alkylidene according to Procedure C provided a solid in 36% yield after flash chromatography (4:1 hexanes:EtOAc) and recrystallization from MeOH. M.p. 88-89 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.27-7.21 (m, 2H), 6.89-6.76 (m, 3H), 3.76 (s, 3H), 3.43 (s, 1H), 2.55-2.40 (m, 2H), 2.10-1.90 (m, 2H), 1.70-1.50 (m, 2H), 1.52-1.30 (m, 4H), 1.47 (s, 3H), 0.81 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 159.9, 141.4, 129.6, 120.0, 113.9, 112.5, 105.6, 57.0, 55.2, 47.2, 35.6, 30.5, 26.4, 25.6, 22.3; Anal. Calcd for C₁₉H₂₄O₅: C, 68.66; H, 7.28. Found: C, 68.64; H, 7.39.

5-Methoxy-(3.3)-pentamethylene-1-indanone (56) and 7-Methoxy-(3.3)-pentamethylene-1-indanone¹⁴ (57): Prepared from **55** in 71% yield as a 3.4:1 ratio of para **56**:ortho **57** products using Procedure D in 120 min. The mixture was separated with 3:1 hexanes:EtOAc; (**56**): M.p. 82-82.5 °C (hexanes). Lit. 83.5-85 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.60 (d, *J* = 9.0 Hz, 1H), 6.87-6.84 (m, 2H), 3.86 (s, 3H), 2.53 (s, 2H), 1.77-1.26 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz) δ 204.2, 167.1, 165.3, 128.8, 125.1, 115.1, 107.4, 55.6, 48.5, 42.9, 38.2, 25.4, 23.7. Anal. calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88. Found: C, 78.38; H, 7.84. (**57**): M.p. 94-96 °C. Lit. 97.5-99 °C (Et₂O); ¹H NMR (CDCl₃, 300 MHz) δ 7.52 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 2.55 (s, 2H), 1.77-1.25 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz) δ 203.9, 167.0, 157.6, 136.5, 123.6, 115.6, 108.8, 55.8, 48.9, 42.5, 38.3, 25.5, 23.7. HRMS(EI): *m/z* calcd for C₁₅H₁₈O₂ (M⁺): 230.1307. Found: 230.1304.

2,2-Dimethyl-5-(3-methylbenzyl)-1,3-dioxane-4,6-dione (58): Reductive alkylation of Meldrum's acid with *m*-tolualdehyde according to Procedure A provided a white solid in 69% yield following

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recrystallization from MeOH. M.p. 81-82.5 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.15-7.01 (m, 4H), 3.76 (t, J = 4.9 Hz, 1H), 3.41 (d, J = 4.9 Hz, 2H), 2.30 (s, 3H), 1.71 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.3, 138.1, 137.1, 130.3, 128.3, 127.7, 126.5, 105.1, 47.9, 31.8, 38.3, 27.0, 21.2; Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{O}_4$: C, 67.73; H, 6.50. Found: C, 67.67; H, 6.46.

5-Methyl-1-indanone (59) and 7-Methyl-1-indanone¹⁵ (60): Prepared from **58** in 48% yield as a 1:1 ratio of para **59**:ortho **60** products using Procedure D in 60 min. The mixture was separated with 10:1 hexanes:EtOAc; (**59**): M.p 67-68 °C (petroleum ether). Lit. 68-69 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.62 (d, J = 7.8 Hz, 1H), 7.25 (br s, 1H), 7.15 (d, J = 7.9 Hz, 1H), 3.08-3.04 (m, 2H), 2.67-2.63 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 206.6, 155.7, 145.7, 134.8, 128.5, 127.0, 123.5, 36.4, 25.6, 22.0. HRMS(EI): m/z calcd for $\text{C}_{10}\text{H}_{10}\text{O}$ (M^+): 146.0732. Found: 146.0732. (**60**): M.p. 49-50 °C (petroleum ether). Lit. 52.5-53.5 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.38 (t, J = 7.5 Hz, 1H), 7.23 (d, J = 7.4 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 3.05-3.01 (m, 2H), 2.62-2.58 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.8, 155.8, 138.6, 134.3, 133.8, 128.9, 123.9, 36.6, 25.2, 18.2. HRMS(EI): m/z calcd for $\text{C}_{10}\text{H}_{10}\text{O}$ (M^+): 146.0732. Found: 146.0728.

2,2-Dimethyl-5-[1-(3-methylphenyl)cyclohexyl]-1,3-dioxane-4,6-dione (61): Prepared by conjugate addition of 3-methylphenylmagnesium bromide to cyclohexyl Meldrum's alkylidene according to Procedure C. A white solid was obtained in 35 % yield after flash chromatography (5:1 hexanes:EtOAc) and recrystallization from MeOH. M.p. 124-125 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.21-6.90 (m, 4H), 3.42 (s, 1H), 2.50-2.40 (m, 2H), 2.28 (s, 3H), 2.00-1.90 (m, 2H), 1.75-1.55 (m, 2H), 1.44 (s, 3H), 1.44-1.30 (m, 4H), 0.69 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.3, 139.6, 138.1, 128.5, 128.1, 127.9, 124.6, 105.5, 56.9, 47.0, 35.5, 30.5, 26.1, 25.6, 22.2, 21.5; Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_4$: C, 72.13; H, 7.65. Found: C, 72.09; H, 7.63.

5-Methyl-(3.3)-pentamethylene-1-indanone (62) and 7-Methyl-(3.3)-pentamethylene-1-indanone (63): Prepared from **61** in 62% yield as a 1:1 ratio of para **62**:ortho **63** products using Procedure D in 120 min. The resulting mixture of **62** and **63** was separated with 10:1 hexanes:EtOAc; (**62**): M.p. 77.5-78.5 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.58 (d, J = 7.8 Hz, 1H), 7.27 (s, 1H), 7.15 (d, J = 7.8 Hz, 1H), 2.55 (s, 2H), 2.43 (s, 3H), 1.79-1.27 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.6, 164.7, 145.9, 133.3, 128.8, 124.3, 123.2, 48.5, 42.9, 38.3, 25.5, 23.8, 22.2. HRMS(EI): m/z calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ (M^+) 214.1358. Found 214.1354. (**63**): Oil; ^1H NMR (CDCl_3 , 300 MHz) δ 7.42 (t, J = 7.5 Hz, 1H), 7.29

(d, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 2.61 (s, 3H), 2.53 (s, 2H), 1.78-1.23 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.1, 165.1, 138.5, 134.0, 133.0, 129.3, 121.2, 48.9, 42.3, 38.5, 25.5, 23.8, 18.4. Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.07; H, 8.47. Found: C, 84.19; H, 8.36.

5-(3-Chlorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (64): Reductive alkylation of Meldrum's acid with 3-chlorobenzaldehyde according to Procedure A produced white needles in 51% yield following recrystallization from MeOH. M.p. 105-105 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.31 (s, 1H), 7.19 (s, 3H), 3.74 (t, $J = 5.0$ Hz, 1H), 3.41 (d, $J = 5.0$ Hz, 2H), 1.73 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.9, 139.2, 134.2, 129.8, 128.0, 127.3, 105.2, 47.9, 31.3, 28.4, 26.9. HRMS(EI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{ClO}_4$ (M^+): 268.0502. Found 268.0493.

5-[1-(3-Chlorophenyl)cyclohexyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (65): Conjugate addition of 3-chlorophenylmagnesium bromide to cyclohexyl Meldrum's alkylidene according to Procedure C provided a 51% yield of a white solid following flash chromatography (4:1 hexanes:EtOAc) and recrystallization from MeOH. M.p. 115-116 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.14 (m, 4H), 3.44 (s, 1H), 2.50-2.30 (m, 2H), 2.10-1.90 (m, 2H), 1.75-1.65 (m, 2H), 1.48 (s, 3H), 1.48-1.30 (m, 4H), 0.88 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.2, 142.1, 134.7, 129.9, 128.0, 127.5, 126.0, 105.6, 56.9, 47.0, 35.4, 30.4, 26.4, 25.5, 22.2; Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{ClO}_4$: C, 64.19; H, 6.28. Found: C, 64.16; H, 6.39.

5-Chloro-(3.3)-pentamethylene-1-indanone (66) and 7-Chloro-(3.3)-pentamethylene-1-indanone (67): Prepared from **65** in 62% yield as a 2:1 ratio of para **66**:ortho **67** products using Procedure D in 120 min. The mixture was separated with 3:1 CH_2Cl_2 :hexanes; (**66**): M.p. 74-75 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.61 (d, $J = 8.2$ Hz, 1H), 7.46 (d, $J = 1.6$ Hz, 1H), 7.30 (dd, $J = 8.1, 1.6$ Hz, 1H), 2.57 (3H, s), 1.80-1.22 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 204.5, 165.6, 141.2, 134.0, 128.3, 124.7, 124.4, 48.3, 43.2, 38.2, 25.3, 23.7. HRMS(EI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}$ (M^+) 234.0811. Found 234.0807. (**67**): M.p. 159-160 °C (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.48 (t, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 7.5$ Hz, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 2.60 (s, 2H), 1.80-1.24 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 202.8, 166.5, 135.1, 131.5, 131.3, 129.1, 122.4, 48.9, 42.3, 38.4, 25.4, 23.7. HRMS(EI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}$ (M^+): 234.0811. Found 234.0806.

5-(3,5-Dimethoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (68): Prepared by alkylation of **9** according to Procedure B using iodomethane. Recrystallization from *i*-PrOH provided a white solid in

79% yield. M.p. 113-114 °C (*i*-PrOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.24 (s, 3H), 3.64 (s, 6H), 3.18 (s, 2H), 1.65 (s, 3H), 1.53 (s, 3H), 0.94 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.6, 160.7, 137.3, 107.6, 105.1, 99.9, 55.1, 51.9, 44.7, 29.1, 28.3, 26.1; Anal. Calcd for C₁₆H₂₀O₆: C, 62.33; H, 6.54. Found: C, 62.29; H, 6.58.

5,7-Dimethoxy-2-methyl-1-indanone¹⁶ (69): Prepared from **68** in 80% yield using Procedure D in 45 min. Purified with 1:1 hexanes:EtOAc; M.p. 71.5-73 °C (hexanes). Lit. 76-79 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.44 (br s, 1H), 6.28 (br s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.21-3.29 (m, 1H), 2.69-2.55 (m, 2H), 1.25 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.6, 166.9, 159.5, 158.6, 118.5, 101.5, 97.4, 55.7, 42.3, 35.0, 17.1. Anal. Calcd. for C₁₂H₁₄O₃: C, 69.88; H, 6.84. Found: C, 69.58; H, 6.71.

5-(3,5-Dimethylbenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (70): Alkylation of **23** according to Procedure B using iodomethane, followed by recrystallization from MeOH gave a 38% yield of white crystals. M.p. 117-118 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.83 (s, 1H), 6.75 (s, 2H), 3.22 (s, 2H), 2.21 (s, 6H), 1.71 (s, 3H), 1.57 (s, 3H), 0.88 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.8, 138.2, 135.1, 129.2, 127.7, 105.3, 52.1, 44.7, 29.3, 28.2, 26.0, 21.1; HRMS(EI) *m/z* calcd for C₁₆H₂₀O₄ (M⁺): 276.1361. Found: 276.1365.

2,5,7-Trimethyl-1-indanone¹⁷ (71): Prepared from **70** in 87% yield using Procedure D in 30 min. Purified by flash chromatography (10:1 hexanes:EtOAc) to provide a clear colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.24 (s, 1H), 6.85 (s, 1H), 3.23 (dd, *J* = 18.3, 9.3 Hz, 1H), 2.62-2.53 (m, 5H), 2.33 (s, 3H), 1.24 (d, *J* = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 209.6, 154.5, 144.9, 138.5, 131.3, 130.2, 124.1, 42.2, 34.2, 21.7, 18.0, 16.4; HRMS(EI) *m/z* calcd for C₁₂H₁₄O (M⁺): 174.1045. Found: 174.1040.

5-(3,4-Dimethoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (72): Prepared by alkylation of **27** according to Procedure B using iodomethane. Recrystallization from MeOH provided a white solid in 76% yield. M.p. 88-89 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.68-6.60 (m, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 3.18 (s, 2H), 1.64 (s, 3H), 1.52 (s, 3H), 0.90 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.8, 148.7, 148.3, 127.6, 122.1, 112.8, 110.9, 105.0, 55.6, 52.2, 44.3, 29.1, 28.3, 25.7; Anal. Calcd for C₁₆H₂₀O₆: C, 62.33; H, 6.54. Found: C, 62.68; H, 6.68.

5,6-Dimethoxy-2-methyl-1-indanone¹⁸ (73): Prepared from **72** in 77% yield using Procedure D in 45 min. Purified by flash chromatography (2:1 hexanes:EtOAc) to provide a white powder. M.p. 131-132 °C (CH₂Cl₂). Lit. 132-133 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.08 (s, 1H), 6.79 (s, 1H), 3.88 (s, 1H), 3.82

(s, 1H), 3.22 (dd, $J = 16.4, 7.2$ Hz, 1H), 2.64-2.51 (m, 2H), 1.20 (d, $J = 7.2$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.9, 155.3, 149.3, 148.5, 128.8, 107.3, 104.3, 56.0, 55.9, 42.0, 34.6, 16.5; HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$ (M^+): 206.0943. Found: 206.0941.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-5-phenyl-1,3-dioxane-4,6-dione (74): Phenyl Meldrum's acid¹⁹ was alkylated with 3,4-dimethoxybenzyl bromide²⁰ according to Procedure B and purified by recrystallization from MeOH to provide a white solid in 68% yield. M.p. 99-100 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.59-7.56 (m, 2H), 7.40-7.36 (m, 3H), 6.88-6.85 (m, 2H), 6.76-6.74 (m, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.61 (s, 2H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 167.0, 148.5, 148.3, 136.1, 129.4, 128.8, 127.6, 126.5, 123.3, 114.0, 110.9, 105.4, 61.9, 55.8, 55.7, 45.1, 28.9, 28.4; HRMS(EI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{O}_6$ (M^+): 370.1416. Found: 370.1411.

5,6-Dimethoxy-2-phenyl-1-indanone²¹ (75): Prepared from **74** in 67% yield using Procedure D in 60 min. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a white solid. M.p. 155-157 °C (MeOH). Lit. 153-156 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.31-7.13 (m, 6H), 6.92 (s, 1H), 3.97 (s, 3H), 3.89 (s, 3H), 3.84 (dd, $J = 8.0, 3.5$ Hz), 3.57 (dd, 17.2, 8.0 Hz, 1H), 3.13 (dd, $J = 17.2, 3.5$ Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 204.6, 155.7, 149.6, 149.9, 140.2, 128.9, 128.7, 127.7, 126.8, 107.2, 104.7, 56.2, 56.1, 53.6, 35.7; HRMS(EI) m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$ (M^+): 268.1099. Found: 268.1107.

5-Benzyl-5-(3,4-dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (76): Prepared by the alkylation of **27** according to Procedure B using benzyl bromide. Recrystallization from EtOH provided a clear colorless solid in 70% yield. M.p. 148-149 °C (EtOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.24-7.14 (m, 5H), 6.73-6.70 (m, 3H), 3.80 (s, 3H), 3.77 (s, 3H), 3.38 (s, 2H), 3.37 (s, 2H), 0.70 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 168.2, 148.8, 148.4, 134.7, 129.9, 129.6, 128.6, 128.3, 127.6, 127.2, 122.2, 113.0, 111.1, 105.6, 60.0, 55.7, 44.8, 44.4, 28.7, 28.3; Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}_6$: C, 68.74; H, 6.29. Found: C, 68.52; H, 6.34.

2-Benzyl-5,6-dimethoxy-1-indanone²² (77): Prepared from **76** in 80% yield using Procedure D in 45 min. Purified by flash chromatography (2:1 hexanes:EtOAc) to provide a white solid. M.p. 125-126 °C (CH_2Cl_2). Lit. 125-126 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.28-7.16 (m, 5H), 7.16 (s, 1H), 6.77 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.33 (dd, $J = 14.0, 4.0$ Hz, 1H), 3.07-2.94 (m, 2H), 2.73 (dd, $J = 16.3, 2.7$ Hz, 1H), 2.60 (dd, $J = 13.9, 10.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 206.3, 155.6, 149.5, 148.8, 139.7,

129.2, 128.8, 128.4, 126.2, 107.4, 104.4, 56.1, 56.0, 49.1, 37.2, 31.8; HRMS m/z calcd for $C_{18}H_{18}O_3$ (M^+): 282.1256. Found: 282.1256.

5-Allyl-5-(3,4-dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (78): The alkylation of **27** according to Procedure B using allyl bromide provided a white crystals in 67% yield following recrystallization from EtOH. M.p. 81-82 °C (EtOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.72-6.64 (m, 3H), 5.70-5.56 (m, 1H), 5.19-5.11 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.21 (s, 2H), 2.78 (d, $J = 7.4$ Hz, 2H), 1.48 (s, 3H), 0.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.4, 148.9, 148.5, 130.5, 127.5, 122.3, 121.2, 113.1, 111.2, 105.7, 58.0, 55.8, 44.2, 43.3, 29.4, 29.0; Anal. Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.46; H, 6.73.

2-Allyl-5,6-dimethoxy-1-indanone (79): Prepared from **78** in 76% yield using Procedure D in 45 min. Purified by flash chromatography (2:1 hexanes:EtOAc) to provide a pale yellow oil. 1H NMR ($CDCl_3$, 300 MHz) δ 7.07 (s, 1H), 6.78 (s, 1H), 5.77-5.63 (m, 1H), 5.01 (d, $J = 17.0$ Hz, 1H), 4.94 (d, $J = 10.0$ Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.09 (dd, $J = 17.7, 7.9$ Hz, 1H), 2.71-2.55 (m, 3H), 2.20-2.10 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206.4, 155.4, 149.3, 148.8, 135.4, 129.2, 116.6, 107.3, 104.2, 56.0, 55.9, 46.6, 35.6, 31.6; HRMS m/z calcd for $C_{14}H_{16}O_3$ (M^+): 232.1099. Found: 232.1093.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-5-(2-propynyl)-1,3-dioxane-4,6-dione (80): Prepared by alkylation of **27** according to Procedure B using propargyl bromide. Recrystallization from MeOH gave a white powder in 75% yield. M.p. 121-122 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.74-6.60 (m, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.17 (s, 2H), 2.95 (d, $J = 2.7$ Hz, 2H), 2.12 (t, $J = 2.6$ Hz, 1H), 1.61 (s, 3H) 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 148.8, 148.6, 126.4, 122.1, 112.7, 111.1, 106.3, 78.0, 72.9, 56.7, 55.7, 55.7, 44.0, 29.9, 28.4, 28.1; HRMS(EI) m/z calcd for $C_{18}H_{20}O_6$ (M^+): 332.1260. Found: 332.1251.

5,6-Dimethoxy-2-(2-propynyl)-1-indanone (81): Prepared from **80** in 80% yield using Procedure D in 45 min. Purified by flash chromatography (2:1 hexanes:EtOAc) to provide a white solid. M.p. 109-111 °C (CH_2Cl_2); 1H NMR ($CDCl_3$, 300 MHz) δ 7.09 (s, 1H), 6.83 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.22 (dd, $J = 17.0, 7.5$ Hz, 1H), 2.92 (dd, $J = 17.0, 3.6$ Hz, 1H), 2.77-2.64 (m, 2H), 2.45 (ddd, $J = 16.6, 7.9$ Hz, 2.5 Hz), 1.83 (t, $J = 2.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.7, 155.6, 149.4, 148.8, 129.0, 107.3, 104.3, 81.2, 69.3, 56.1, 55.9, 45.7, 31.6, 20.1; HRMS m/z calcd for $C_{14}H_{14}O_3$ (M^+): 230.0943. Found: 230.0948.

4-[5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl]methylbenzonitrile (82):

The alkylation of **27** according to Procedure B using α -bromo-*p*-tolunitrile provided a 79% yield of white powder following recrystallization from MeOH. M.p. 158-159.5 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.49 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.67-6.60 (m, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.37 (s, 2H), 3.31 (s, 2H), 0.65 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 167.7, 148.8, 148.5, 140.0, 132.2, 130.7, 126.5, 122.1, 118.1, 112.8, 111.6, 111.1, 105.8, 59.5, 55.6, 44.5, 44.3, 28.6, 28.5; HRMS(EI) m/z calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_6$ (M^+): 409.1525. Found: 409.1531.

4-[(5,6-Dimethoxy-1-oxo-2,3-dihydro-1H-2-indenyl)methyl]benzonitrile (83): Prepared from **82** in 78% yield using Procedure D with 17 mol % $\text{Sc}(\text{OTf})_3$ in 320 min. Purified by flash chromatography (3:1 hexanes:EtOAc) to provide a pale yellow solid. Recrystallization from methanol afforded clear colorless crystals. M.p. 259-260 °C (MeOH); IR(neat) 2224 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.55 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.15 (s, 1H), 6.78 (s, 1H), 3.91 (s, 1H), 3.88 (s, 3H), 3.35 (dd, J = 13.9, 4.2 Hz, 1H), 3.07 (dd, J = 16.7, 7.5 Hz, 1H), 2.99-2.91 (m, 1H), 2.79-2.63 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 155.8, 149.7, 148.5, 145.4, 132.3, 129.7, 129.0, 118.9, 110.3, 107.3, 104.4, 56.2, 56.1, 48.4, 37.2, 31.7; HRMS(EI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_3$ (M^+): 307.1208. Found: 307.1211.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-5-(4-nitrobenzyl)-1,3-dioxane-4,6-dione (84):

Compound **27** was alkylated according to Procedure B using 4-nitrobenzyl bromide and recrystallized from MeOH to provide a white solid in 81% yield. M.p. 192-193 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 8.09 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 6.71-6.64 (m, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.46 (s, 3H), 3.37 (s, 2H), 0.71 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 167.8, 148.9, 148.7, 142.4, 142.1, 131.0, 126.6, 123.7, 122.3, 112.9, 111.2, 106.0, 59.5, 55.8, 55.7, 44.5, 44.3, 28.9, 28.6; HRMS(EI) m/z calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_8$ (M^+): 429.1424. Found: 429.1418.

5,6-Dimethoxy-2-(4-nitrobenzyl)-1-indanone (85): Prepared from **84** in 81% yield using Procedure D in 250 min. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a pale yellow solid. Recrystallization from MeOH afforded clear, colorless crystals. M.p. 188-190 °C (MeOH); IR(neat) 2361 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 8.15 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.18 (s, 1H), 6.82 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.42 (dd, J = 13.8, 4.1 Hz, 1H), 3.12 (dd, J = 16.6, 7.5 Hz, 1H), 3.16-2.97 (m, 1H), 2.86 (dd, J = 13.8, 9.5 Hz, 1H), 2.73 (dd, J = 16.7, 3.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 75

MHz) δ 205.3, 155.8, 149.6, 148.4, 147.5, 146.7, 129.7, 128.9, 123.7, 107.3, 104.4, 56.2, 56.1, 48.3, 36.9, 31.6; HRMS(EI) m/z calcd for $C_{18}H_{17}NO_5$ (M^+): 327.1107. Found: 327.1105.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-5-(2,3,4,5,6-pentafluorobenzyl)-1,3-dioxane-4,6-dione (86): Compound **27** was alkylated according to Procedure B using 2,3,4,5,6-pentafluorobenzyl bromide and recrystallized from MeOH to provide a white powder in 95% yield. M.p. 169-169.5 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.75-6.66 (m, 3H), 3.80 (s, 6H), 3.44 (s, 2H), 3.35 (s, 2H), 1.50 (s, 3H), 0.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 148.8, 148.5, 147.2 (m), 143.9 (m), 139.0 (m), 135.6 (m), 126.6, 122.7, 113.3, 111.0, 108.5 (m), 105.8, 56.4, 55.6, 41.7, 31.9, 28.9, 28.6; HRMS(EI) m/z calcd for $C_{22}H_{19}F_5O_6$ (M^+): 474.1102. Found: 474.1108.

5,6-Dimethoxy-2-(2,3,4,5,6-pentafluorobenzyl)-1-indanone (87): Prepared from **86** in 80% yield using Procedure D in 85 min. Purified by flash chromatography (6:1 hexanes:EtOAc) to provide a white solid. M.p. 163-164 °C (CH_2Cl_2); 1H NMR ($CDCl_3$, 300 MHz) δ 7.17 (s, 1H), 6.83 (s, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.29 (dd, J = 13.7 Hz, 5.4 Hz, 1H), 3.14 (dd, J = 16.8, 7.5 Hz, 1H), 2.97-2.94 (m, 1H), 2.90-2.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.3, 155.8, 149.6, 148.1, 146.8 (m), 143.6 (m), 141.5 (m), 139.3-138.2 (m), 135.9-135.7 (m), 128.6, 113.1 (m), 107.3, 104.4, 56.1 (d, J = 7.5 Hz), 46.7 (d, J = 15.0 Hz), 32.1, 24.3; HRMS(EI) m/z calcd for $C_{18}H_{13}F_5O_3$ (M^+): 372.0785. Found: 372.0782.

5-[1-(3,5-Dimethoxyphenyl)ethyl]-2,2,5-trimethyl-1,3-dioxane-4,6-dione (88): Alkylation of **11** according to Procedure B using iodomethane, followed by flash chromatography (4:1 hexanes:EtOAc) and recrystallization from MeOH gave a 60% yield of a white solid. M.p. 72-73 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 6.30 (s, 3H), 3.71 (s, 6H), 3.41 (q, J = 7.2 Hz, 1H), 1.63 (s, 3H), 1.54 (s, 3H), 1.51 (d, J = 7.2 Hz, 3H), 1.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.4, 168.6, 160.7, 142.7, 106.5, 104.9, 100.0, 55.3, 54.0, 48.6, 30.0, 27.6, 22.5, 15.2; HRMS(EI) m/z calcd for $C_{17}H_{22}O_6$ (M^+): 322.1416. Found: 322.1424.

5,7-Dimethoxy-2,3-dimethyl-1-indanone²³ (89): Prepared from **88** in 91% yield as a 5.6:1 mixture of *trans:cis* isomers using Procedure D in 155 min. Purified by flash chromatography (6:1 hexanes:EtOAc) to provide a mixture of *trans:cis* isomers (5.6:1) as a clear, colorless oil. *Trans* isomer: 1H NMR ($CDCl_3$, 300 MHz) δ 6.42 (s, 1H), 6.26 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.71-2.77 (m, 1H), 2.11-2.19 (m, 1H), 1.33 (d, J = 7.1 Hz, 3H), 1.19 (J = 6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 204.4, 167.0, 162.9, 159.1, 117.8, 100.2, 97.2, 55.7, 55.6, 51.5, 41.6, 19.4, 15.0. *Cis* isomer: 1H NMR ($CDCl_3$,

300 MHz) δ 6.42 (s, 1H), 6.26 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.35-3.29 (m, 1H), 2.19-2.11 (m, 1H), 1.16 (d, $J = 7.3$ Hz, 3H), 1.12 ($J = 7.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.1, 166.8, 164.2, 159.1, 117.4, 100.6, 97.2, 55.7, 55.6, 46.6, 36.6, 16.8; HRMS(EI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ (M^+)(mixture of isomers): 220.1099. Found: 220.1095.

5-Benzyl-5-[1-(3,5-dimethoxyphenyl)ethyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (90):

Alkylation of **11** according to Procedure B using benzyl bromide, followed by flash chromatography (4:1 hexanes:EtOAc) and recrystallization from MeOH gave a 67% yield of a white powder. M.p. 125-126 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.24-7.13 (m, 5H), 6.32-6.29 (m, 3H), 3.69 (s, 6H), 3.57 (q, $J = 7.2$ Hz, 1H), 3.55 (d, $J = 12.5$ Hz, 1H), 3.18 (d, $J = 12.5$ Hz, 1H), 1.62 (d, $J = 7.2$ Hz, 3H), 0.67 (s, 3H), 0.48 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 168.5, 166.8, 160.7, 142.5, 135.2, 130.5, 128.6, 127.5, 106.4, 105.6, 99.9, 61.8, 55.2, 48.7, 41.5, 28.9, 27.8, 15.5; HRMS(EI) m/z calcd for $\text{C}_{23}\text{H}_{26}\text{O}_6$ (M^+): 398.1729. Found: 398.1728.

2-Benzyl-5,7-dimethoxy-3-methyl-1-indanone (91): Prepared from **90** in 92% yield as a 12.3:1 mixture of *trans:cis* isomers using Procedure D with 17 mol % $\text{Sc}(\text{OTf})_3$ in 32 hours. Purified by flash chromatography (6:1 hexanes:EtOAc) to provide a mixture of *trans:cis* isomers (12.3:1) as a pale yellow oil. *Trans* isomer: ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.16 (m, 1H), 6.34 (s, 1H), 6.29 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.33 (dd, $J = 13.6, 4.3$ Hz, 1H), 2.92-2.96 (m, 1H), 2.67 (dd, $J = 13.6, 9.9$ Hz, 1H), 2.46-2.51 (m, 1H), 1.06 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 202.7, 167.0, 163.2, 159.1, 139.7, 128.9, 128.2, 126.0, 117.7, 100.2, 97.2, 57.9, 55.6, 55.5, 38.3, 36.5, 20.1. *Cis* isomer: ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.16 (m, 1H), 6.47 (s, 1H), 6.44 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.33 (dd, $J = 13.6, 4.3$ Hz, 1H), 2.96-2.92 (m, 1H), 2.67 (dd, $J = 13.6, 9.9$ Hz, 1H), 2.51-2.46 (m, 1H), 1.13 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 202.4, 166.7, 164.0, 140.5, 128.9, 127.9, 125.7, 117.0, 100.7, 97.2, 60.2, 55.0, 52.9, 31.1, 20.9, 18.7, 14.0; HRMS(EI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3$ (M^+)(mixture of isomers): 296.1412. Found: 296.1407.

5-(2,5-Dimethoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (92): Alkylation of **32** according to Procedure B using iodomethane produced a white solid in 61% yield after recrystallization from MeOH. M.p. 76-77 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.75-6.67(3H, m), 3.71 (3H, s), 3.69 (3H, s), 3.27 (2H, s), 1.66 (3H, s), 1.61 (3H, s), 1.32 (3H, s); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.4, 153.3, 124.0, 117.8,

113.9, 111.3, 104.8, 55.7, 55.4, 50.1, 40.8, 30.0, 27.9, 23.7; HRMS(EI) m/z calcd for $C_{16}H_{20}O_6$ (M^+): 308.1260. Found: 308.1259.

4,7-Dimethoxy-2-methyl-1-indanone²⁴ (93): Prepared from **92** in 69% yield using Procedure D in 20 min. Purified by flash chromatography (5:1 hexanes:EtOAc) to provide a white solid. M.p. 78-79 °C (Et₂O). Lit. 79.5-82.5 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.89 (d, J = 8.7 Hz, 1H), 6.64 (d, J = 8.7 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.16 (dd, J = 17.5, 7.7 Hz, 1H), 2.59-2.43 (m, 2H), 1.19 (d, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 207.2, 151.8, 150.3, 144.1, 125.4, 116.5, 109.5, 55.8, 42.0, 42.1, 31.2, 16.7; HRMS(EI) m/z calcd for $C_{12}H_{14}O_3$ (M^+): 206.0943. Found: 206.0937.

5-(2-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-5-methoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (94): Alkylation of **34** according to Procedure B using iodomethane was followed by flash chromatography using 5:1 (hexanes: EtOAc) to afford a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.75–7.70 (m, 4H), 7.40-7.34 (m, 6H), 6.69-6.68 (m, 1H), 6.31-6.30 (m, 2H), 3.62 (s, 3H), 3.48 (s, 2H), 1.78 (s, 3H), 1.66 (s, 3H), 1.33 (s, 3H), 1.14 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.7, 153.1, 147.5, 135.3, 132.5, 129.7, 127.6, 125.2, 119.9, 115.7, 113.6, 104.9, 55.3, 50.6, 39.5, 30.0, 27.8, 26.4, 23.8, 19.2; HRMS(EI) m/z calcd for $C_{31}H_{36}O_6Si$ (M^+): 532.2281. Found: 532.2278.

4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-7-methoxy-2-methyl-1-indanone (95): Prepared from **94** in 94% yield using Procedure D in 20 min. Purified by flash chromatography (4:1 hexanes:EtOAc) to provide a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.67 (d, J = 6.5 Hz, 4H), 7.45-7.33 (m, 6H), 6.61 (d, J = 8.7 Hz, 1H), 6.36 (d, J = 8.7 Hz, 1H), 3.77 (s, 3H), 3.37-3.29 (m, A of AB, 1H), 2.65 (m, 1H), 2.56 (m, B of AB, 1H), 1.26 (3H, d, J = 7.3 Hz), 1.11 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 207.3, 152.2, 146.1, 145.5, 135.4, 132.5, 130.1, 127.9, 125.2, 125.1, 109.4, 55.8, 42.1, 31.9, 26.5, 19.5, 16.8; HRMS(EI) m/z calcd for $C_{27}H_{30}O_3Si$ (M^+): 430.1964. Found: 430.1967.

5-(2,3-Dimethoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (96): Alkylation of **36** according to Procedure B using iodomethane, followed by flash chromatography (6:1 hexanes:EtOAc) produced a 50% yield of white solid. M.p. 72-73 °C (CH₂Cl₂); ¹H NMR (CDCl₃, 300 MHz) δ 6.92 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 6.73 (d, J = 1.5 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.32 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.5, 152.6, 147.9, 128.5, 123.5, 112.5, 105.1, 60.5, 55.6, 50.3, 40.1, 29.9, 28.1, 24.6; HRMS(EI) m/z calcd for $C_{16}H_{20}O_6$ (M^+): 308.1260. Found: 308.1249.

4,5-Dimethoxy-2-methyl-1-indanone²⁵ (97): Prepared from **96** in 75% yield using Procedure D in 20 min. Purified by flash chromatography (7:1 hexanes:EtOAc) to provide a white solid. M.p. 69-70 °C (Et₂O); ¹H NMR (CDCl₃, 300 MHz) δ 7.49 (d, *J* = 8.3 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.36 (dd, *J* = 18.2, 8.8 Hz, 1H), 2.69-2.60 (m, 2H), 1.25 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 207.8, 157.6, 146.1, 145.3, 130.3, 120.4, 112.3, 60.3, 56.2, 42.1, 31.5, 16.5; HRMS(EI) *m/z* calcd for C₁₂H₁₄O₃ (M⁺): 206.0943. Found: 206.0947.

5-(2-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-3-methoxybenzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (98): Alkylation of **42** according to Procedure B using iodomethane was followed by flash chromatography (5:1 hexanes:EtOAc) and recrystallization from MeOH to give an 84% yield of white powder. M.p. 131-132 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.68-7.65 (m, 4H), 7.33-7.27 (m, 6H), 6.71 (t, *J* = 3.1 Hz, 2H), 6.39 (dd, *J* = 6.1, 3.5 Hz, 1H), 3.64 (s, 2H), 2.73 (s, 3H), 1.75 (s, 3H), 1.66 (s, 3H), 1.35 (s, 3H), 1.10 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.7, 149.4, 143.6, 135.0, 134.3, 128.8, 127.1, 125.5, 121.9, 120.7, 110.7, 104.9, 52.4, 51.0, 37.0, 30.0, 28.0, 27.0, 24.3, 20.0; HRMS(EI) *m/z* calcd for C₃₁H₃₆O₆Si (M⁺-CH₃): 517.2046. Found: 517.2039.

4-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-5-methoxy-2-methyl-1-indanone (99): Prepared from **98** in 86% yield using Procedure D in 30 min. Purified by flash chromatography (11:1 hexanes:EtOAc) to provide a clear colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.84 (dd, *J* = 6.3, 1.2 Hz, 4H), 7.53-7.40 (m, 7H), 3.54 (d, *J* = 8.3 Hz, 1H), 3.54 (q, *J* = 9.4 Hz, 1H), 3.25 (s, 3H), 2.84-2.76 (m, 2H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.27 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 208.3, 154.6, 144.0, 141.4, 134.7, 134.1, 130.2, 129.4, 127.3, 117.9, 111.6, 54.4, 42.1, 32.2, 26.7, 20.0, 16.5; HRMS(EI) *m/z* calcd for C₂₇H₃₀O₃Si (M⁺-CH₃): 415.1724. Found: 415.1735.

5-(3-Methoxy-2-[(1,1,1-triisopropylsilyl)oxy]benzyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (100): Alkylation of **23** according to Procedure B using iodomethane, followed by flash chromatography (8:1 hexanes:EtOAc) provided a white solid. M.p. 60-61 °C (Benzene); ¹H NMR (CDCl₃, 300 MHz) δ 6.74-6.61 (m, 3H), 3.71 (s, 3H), 3.45 (s, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.30 (s, 3H), 1.30-1.23 (septet, *J* = 7.3 Hz, 3H), 1.06 (d, *J* = 7.2 Hz, 18H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.6, 149.9, 144.4, 125.8, 122.0, 120.1, 110.3, 104.7, 54.6, 50.5, 39.0, 29.9, 28.0, 24.2, 18.1, 14.2; HRMS(EI) *m/z* calcd for C₂₄H₃₈O₆Si (M⁺-CH₃): 435.2203. Found: 435.2218.

5-Methoxy-2-methyl-4-[(1,1,1-triisopropylsilyl)oxy]-1-indanone (101): Prepared from **100** in 77% yield using Procedure D in 40 min. Purified by flash chromatography (10:1 hexanes:EtOAc) to provide a pale yellow oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.36 (d, J = 8.3 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.85 (s, 2H, s), 3.32 (dd, J = 16.8, 7.6 Hz, 1H), 2.64-2.59 (m, 2H), 1.25 (septet, J = 6.8 Hz, 6H), 1.07 (d, J = 7.1 Hz, 18H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 208.3, 155.0, 144.3, 142.1, 130.4, 117.4, 111.5, 55.3, 42.2, 32.2, 18.0, 16.6, 13.7; HRMS(EI) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{Si}$ (M^+): 348.2121. Found: 348.2129.

5,5-Dibenzyl-2,2-dimethyl-1,3-dioxane-4,6-dione²⁶ (102): Prepared according to Procedure B from Meldrum's acid and benzyl bromide. The reaction mixture in DMF was poured into H_2O and stirred vigorously for 10 minutes, and the resulting white solid was filtered and dried under high vacuum to provide a white powder in 90% yield. M.p. 225-227 °C (H_2O); ^1H NMR (CDCl_3 , 300 MHz) δ 7.25-7.17 (m, 10H), 3.42 (s, 4H), 0.60 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 168.1, 134.8, 130.1, 128.7, 127.7, 105.8, 60.0, 44.8, 28.5; Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$: C, 74.06; H, 6.21. Found: C, 73.97; H, 6.18.

2-Benzyl-1-indanone²⁵ (103): Prepared from **102** in 66% yield using Procedure D in 50 min. Using catalytic TfOH gave 71% yield in the same time period. Purified by flash chromatography (10:1 hexanes:EtOAc) to provide a clear colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 7.77 (d, J = 7.6 Hz, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.38-7.20 (m, 7H), 3.39 (dd, J = 4.2, 3.9 Hz, 1H), 3.15 (dd, J = 17.0, 7.7 Hz, 1H), 3.10-2.90 (m, 1H), 2.84 (dd, J = 17.0, 3.9 Hz, 1H), 2.65 (dd, J = 13.9, 10.4 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 207.7, 153.5, 139.6, 136.5, 134.7, 128.8, 128.4, 127.3, 126.5, 126.3, 123.9, 48.8, 36.9, 32.1; HRMS(EI) m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}$ (M^+): 222.1045. Found: 222.1052.

5,5-Di(4-fluorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (104): The dialkylation of Meldrum's acid with 4-fluorobenzyl bromide was performed according to Procedure B. The product was precipitated by addition of water, then filtered and dried under high vacuum. Recrystallization from MeOH provided a white solid in 74% yield. M.p. 144-145 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.16-7.11 (m, 4H), 6.96-6.90 (m, 4H), 3.67 (s, 4H), 0.68 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 168.0, 164.0, 160.7, 131.8, 131.7, 130.5, 115.8, 105.9, 60.0, 43.9, 28.7; HRMS(EI) m/z calcd for $\text{C}_{20}\text{H}_{18}\text{F}_2\text{O}_4$ (M^+): 360.1173. Found: 360.1166.

2,2-Dimethyl-5,5-di(4-nitrobenzyl)-1,3-dioxane-4,6-dione²⁶ (106): The dialkylation of Meldrum's acid with 4-nitrobenzyl bromide was performed according to Procedure B. The product was precipitated by addition of water, then filtered and dried under high vacuum. Recrystallization from MeOH provided a

white solid in 89% yield. M.p. 237-238 °C (MeOH). Lit. 258-259 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.16 (d, *J* = 8.6 Hz, 4H), 7.38 (d, *J* = 8.6 Hz, 4H), 3.56 (s, 4H), 0.72 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.3, 147.7, 141.6, 131.3, 130.9, 124.0, 123.8, 106.3, 59.0, 44.4, 29.0.

5,5-Di(3-fluorobenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (108): Dialkylation of Meldrum's acid according to Procedure B with 3-fluorobenzyl bromide to provide a white solid in a yield of 58% after recrystallization from MeOH. M.p. 137-138 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.27-7.19 (m, 2H), 7.00-6.88 (m, 6H), 3.40 (s, 4H), 0.71 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.8, 164.4, 161.1, 136.9, 130.3, 125.9, 117.2 (d, *J* = 22.5 Hz), 114.9 (d, *J* = 15.0 Hz), 106.0, 59.5, 44.5, 28.7; HRMS(EI) *m/z* calcd for C₂₀H₁₈F₂O₄ (M⁺): 360.1173. Found: 360.1177.

5-Fluoro-2-(3-fluorobenzyl)-1-indanone (109): Prepared from **108** in 93% yield as a 13:1 mixture of para **109**:ortho **110** products using Procedure D in 90 min. The mixture was separated by flash chromatography (13:1 hexanes:EtOAc) to provide clear colorless oils. ¹H NMR (CDCl₃, 300 MHz) δ 7.78-7.74 (m, 1H), 7.24-7.20 (m, 1H), 7.08-6.90 (m, 5H), 3.35 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.17 (dd, *J* = 17.2, 7.8 Hz, 1H), 3.05-2.90 (m, 1H), 2.80 (dd, *J* = 17.1, 4.2 Hz, 1H), 2.68 (dd, *J* = 13.9, 10.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.4, 166.8 (d, *J* = 336.2 Hz), 163.4 (d, *J* = 325.7 Hz), 156.3 (d, *J* = 10.0 Hz), 141.9 (d, *J* = 7.1 Hz), 132.8 (d, *J* = 1.7 Hz), 130.0 (d, *J* = 8.4 Hz), 126.3 (d, *J* = 10.5 Hz), 124.5, 115.8 (d, *J* = 23.7 Hz), 115.7 (d, *J* = 20.9 Hz), 113.4 (d, *J* = 20.9 Hz), 113.2 (d, *J* = 22.1 Hz), 48.8, 36.6, 32.0; HRMS(EI) *m/z* calcd for C₁₆H₁₂F₂O (M⁺): 258.0856. Found: 258.0851.

7-Fluoro-2-(3-fluorobenzyl)-1-indanone (110): ¹H NMR (CDCl₃, 300 MHz) δ 7.80-7.75 (m, 1H), 7.28-7.24 (m, 1H), 7.09-6.92 (m, 5H), 3.36 (dd, *J* = 14.0, 4.3 Hz, 1H), 3.18 (dd, *J* = 17.3, 7.8 Hz, 1H), 3.20-2.99 (m, 1H), 2.84 (dd, *J* = 17.3, 3.9 Hz, 1H), 2.70 (dd, *J* = 14.0, 10.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 203.4, 162.7 (d, *J* = 244.0 Hz), 159.1 (d, *J* = 262.0 Hz), 155.4 (d, *J* = 20.0 Hz), 141.8 (d, *J* = 7.1 Hz), 136.8 (d, *J* = 8.3 Hz), 130.0 (d, *J* = 8.3 Hz), 124.6, 122.4, 115.7 (d, *J* = 20.9 Hz), 114.4 (d, *J* = 19.1 Hz), 113.4 (d, *J* = 20.9 Hz), 49.1, 36.5, 32.0; HRMS(EI) *m/z* calcd for C₁₆H₁₂F₂O (M⁺): 258.0856. Found: 258.0858.

5-[(1-Benzyl-3-piperidyl)methyl]-5-(3,4-dimethoxybenzyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (111): Reductive alkylation of Meldrum's acid according to Procedure A using *N*-benzyl-4-formylpiperidine (prepared by Swern oxidation of (1-benzylpiperidin-4-yl)methanol)²⁷ provided the monosubstituted derivative in 47% yield after flash chromatography (50:1 CH₂Cl₂:MeOH). This yellow oil

was alkylated with 3,4-dimethoxybenzyl bromide²⁰ according to Procedure B, and the target material was isolated as a pale yellow solid in 44% yield following flash chromatography (5:2 EtOAc:hexanes) and recrystallization from MeOH. M.p. 120-121 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.25-7.17 (m, 5H), 6.70-6.64 (m, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.39 (s, 2H), 3.17 (s, 2H), 2.80-2.76 (m, 2H), 2.10-2.07 (m, 2H), 1.84-1.80 (m, 2H), 1.60-1.52 (m, 2H), 1.52 (s, 3H), 1.35-1.20 (m, 3H), 0.65 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.0, 148.9, 148.5, 138.2, 128.9, 128.0, 127.5, 126.8, 122.5, 113.2, 111.2, 105.8, 63.2, 56.2, 55.8, 55.7, 53.3, 47.9, 44.4, 33.2, 32.7, 29.1, 29.1; HRMS(EI) *m/z* calcd for C₂₈H₃₅NO₆ (M⁺): 481.2464. Found: 481.2458.

2-[(1-Benzyl-4-piperidyl)methyl]-5,6-dimethoxy-1-indanone (donepezil) (112): Prepared from **111** in 61% yield using Procedure D with TfOH (1.2 eq) in 30 min. After removal of nitromethane, the crude brown oil was dissolved in CH₂Cl₂ and washed with saturated NaHCO₃ (2 times) then the organic layer washed with brine, then dried over MgSO₄ and filtered. Concentration, followed by flash chromatography (20:1 CH₂Cl₂:MeOH) provided a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.30-7.14 (m, 5H), 7.14 (s, 3H), 6.83 (s, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.51 (s, 2H), 3.21 (dd, *J* = 17.5, 8.1 Hz, 1H), 2.92-2.87 (m, 2H), 2.70-2.63 (m, 2H), 2.02-1.80 (m, 3H), 1.75-1.60 (m, 2H), 1.55-1.20 (m, 4H); ¹³C NMR (CDCl₃, 75 MHz) δ 207.7, 155.4, 149.4, 148.7, 138.1, 129.3, 128.1, 127.0, 107.3, 104.4, 63.3, 56.2, 56.1, 53.7, 45.4, 38.7, 34.3, 33.4, 32.8, 31.7; HRMS(EI) *m/z* calcd for C₂₄H₂₉NO₃ (M⁺): 379.2147. Found: 379.2142.

5-(3,4-Dimethoxybenzyl)-2,2-dimethyl-5-(4-pyridylmethyl)-1,3-dioxane-4,6-dione (113): Alkylation of **27** according to Procedure B with (4-bromomethyl)pyridine hydrobromide provided a 74% yield of an off-white solid after recrystallization from MeOH. M.p. 139-141 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 8.51 (d, *J* = 5.8 Hz, 2H), 7.10 (d, *J* = 5.8 Hz, 2H), 6.74-6.68 (m, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.39 (s, 2H), 3.38 (s, 2H), 0.74 (s, 3H), 0.68 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 167.5, 149.9, 148.6, 148.4, 143.2, 128.4, 124.7, 122.0, 112.7, 110.9, 105.9, 59.1, 55.5, 44.3, 43.6, 28.5, 28.4; HRMS(EI) *m/z* calcd for C₂₁H₂₃NO₆ (M⁺): 385.1525. Found: 385.1522.

5,6-Dimethoxy-2-(4-pyridylmethyl)-1-indanone²⁸ (114): Prepared from **113** using Procedure D, using TfOH (1.2 eq) in 45 min. After removal of nitromethane, the crude brown oil was dissolved in CH₂Cl₂ and washed with saturated NaHCO₃ (2 times), brine, then dried over MgSO₄ and filtered. Concentration, followed by flash chromatography (20:1 CH₂Cl₂:MeOH) provided a pale yellow solid in

77% yield. The use of TMSOTf (1.2 eq) instead of TfOH provided a 62% yield. Recrystallization from MeOH afforded a white powder. M.p. 190-191 °C (MeOH). Lit. 190-191 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.49-8.48 (m, 2H), 7.17-7.14 (m, 3H), 6.79 (s, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.32 (dd, *J* = 14.1 Hz, 4.1 Hz, 1H), 3.09 (dd, *J* = 16.7 Hz, 7.5 Hz, 1H), 3.00-2.90 (m, 1H), 2.71-2.63 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 205.1, 155.4, 149.5, 149.3, 148.5, 148.3, 128.6, 124.0, 107.1, 104.0, 55.9, 55.7, 47.6, 36.1, 31.5; HRMS(EI) *m/z* calcd for C₁₇H₁₇NO₃ (M⁺): 283.1208. Found: 283.1205.

5-(3,4-Dimethoxyphenethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (115): Condensation and reduction of Meldrum's acid and 3,4-dimethoxyphenylacetic acid according to the procedure of Tsukamoto²⁹ provided a white powder in 79% yield after recrystallization from MeOH. M.p. 138-139.5 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.77-6.73 (m, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.46 (t, *J* = 5.3 Hz, 1H), 2.81-2.76 (m, 2H), 2.41-2.36 (m, 2H), 1.74 (s, 3H), 1.72 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.3, 148.8, 147.3, 132.7, 120.4, 111.6, 111.1, 104.7, 55.7, 55.6, 44.8, 31.8, 28.3, 27.9, 26.4; HRMS(EI) *m/z* calcd for C₁₆H₂₀O₆ (M⁺): 308.1260. Found: 308.1257.

6,7-Dimethoxy-1,2,3,4-tetrahydro-1-naphthalenone³⁰ (116): Prepared from **115** in 82% yield using Procedure D in 45 min. Purified by flash chromatography (1:1 hexanes:EtOAc) to provide a white solid. M.p. 96-98 °C (CH₂Cl₂). Lit. 98-99 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.48 (s, 1H), 6.64 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.88-2.84 (m, 2H), 2.58-2.54 (m, 2H), 2.10-2.07 (m, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 197.1, 153.3, 147.8, 139.2, 128.7, 110.1, 108.3, 55.9, 38.4, 29.3, 23.5; HRMS(EI) *m/z* calcd for C₁₂H₁₄O₃: 206.0943. Found: 206.0950.

5-(3,4-Dimethoxyphenethyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione (117): Alkylation of **115** according to Procedure B using iodomethane, followed by recrystallization from MeOH provided an 82% yield of white powder. M.p. 81.5-83 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 6.70-6.57 (m, 3H), 3.76 (s, 6H), 3.74 (s, 3H), 2.43-2.38 (m, 2H), 2.8-2.24 (m, 2H), 1.67 (br s, 6H), 1.57 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.0, 148.7, 147.4, 132.1, 120.0, 111.4, 111.1, 104.7, 55.6, 55.6, 49.2, 42.8, 31.2, 29.5, 28.2, 24.0; HRMS(EI) *m/z* calcd for C₁₇H₂₂O₆ (M⁺): 322.1416. Found: 322.1419.

6,7-Dimethoxy-2-methyl-1,2,3,4-tetrahydro-1-naphthalenone³¹ (118): Prepared from **117** in 82% yield using Procedure D in 15 min. Purified by flash chromatography (3:1 hexanes:EtOAc) to provide a pale yellow solid. M.p. 120-121 °C (CH₂Cl₂). Lit. 129-130 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.49 (s, 1H), 6.62 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.00-2.80 (m, 2H), 2.53-2.45 (m, 1H), 2.18-2.12 (m, 1H),

1.90-1.75 (m, 1H), 1.23 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 199.5, 153.1, 147.1, 138.8, 125.3, 109.9, 108.5, 55.8, 41.7, 31.5, 28.3, 15.4; HRMS(EI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$: 220.1099. Found: 220.1107.

5-[3-(3,4-Dimethoxyphenyl)propyl]-2,2-dimethyl-1,3-dioxane-4,6-dione (119): Condensation and reduction of Meldrum's acid and 3,4-dimethoxyhydrocinnamic acid according to Tsukamoto²⁹ provided a white solid in 68% yield after recrystallization from MeOH. M.p. 113-114.5 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.76-6.67 (m, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.48 (t, $J = 4.9$ Hz, 1H), 2.60 (t, $J = 7.6$ Hz, 2H), 2.14-2.07 (m, 2H), 1.80-1.68 (m, 2H), 1.69 (br s, 6 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.4, 148.7, 147.1, 134.0, 120.1, 111.4, 111.1, 104.7, 55.8, 55.4, 45.9, 35.2, 28.3, 27.8, 26.6, 26.0; HRMS(EI) m/z calcd for $\text{C}_{17}\text{H}_{22}\text{O}_6$ (M^+): 322.1416. Found: 322.1407.

2,3-Dimethoxy-6,7,8,9-tetrahydro-5H-benzo[*a*]cyclohepten-5-one³² (120): Prepared from **119** in 78% yield using Procedure D in 45 min. Purified by flash chromatography (1:1 hexanes:EtOAc) to provide a white solid. M.p. 61-62.5 °C (CH_2Cl_2). Lit. 63-64 °C; ^1H NMR (CDCl_3 , 300 MHz) δ 7.35 (s, 1H), 6.65 (s, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 2.90-2.86 (m, 2H), 2.73-2.69 (m, 2H), 1.87-1.74 (m, 4H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 203.7, 152.0, 147.3, 136.6, 130.6, 112.2, 111.1, 55.8, 40.6, 32.4, 25.0, 20.5; HRMS(EI) m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$: 220.1099 Found: 220.1096.

5-[3-(3,4-Dimethoxyphenyl)propyl]-2,2,5-trimethyl-1,3-dioxane-4,6-dione (121): Alkylation of **119** using Procedure B with iodomethane, followed by recrystallization from MeOH provided a 79% yield of a white powder. M.p. 80-81 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 6.77-6.63 (m, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 2.52 (t, $J = 7.6$ Hz, 2H), 2.06-2.00 (m, 2H), 1.71 (s, 3H), 1.70 (s, 3H), 1.60 (s, 3H), 1.60-1.40 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 170.2, 148.6, 147.1, 133.3, 120.2, 111.2, 111.0, 104.7, 55.7, 55.6, 49.3, 40.5, 34.8, 29.6, 28.3, 27.0, 24.0; HRMS(EI) m/z calcd for $\text{C}_{18}\text{H}_{24}\text{O}_6$ (M^+): 336.1573. Found: 336.1585.

2,3-Dimethoxy-6-methyl-6,7,8,9-tetrahydro-5H-benzo[*a*]cyclohepten-5-one (122): Prepared from **121** in 81% yield using Procedure D in 15 min. Purified by flash chromatography (1:1 hexanes:EtOAc) to provide a pale yellow solid. M.p. 80-81 °C (from CH_2Cl_2); ^1H NMR (CDCl_3 , 300 MHz) δ 7.33 (s, 1H), 6.65 (s, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.05-2.84 (m, 3H), 2.10-1.90 (m, 1H), 1.89-1.82 (m, 1H), 1.70-1.50 (m, 2H), 1.20 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 205.0, 151.2, 147.0, 137.2, 131.3,

112.3, 111.1, 55.8, 43.5, 43.4, 31.2, 25.5, 16.4; HRMS(EI) m/z calcd for $C_{14}H_{18}O_3$: 234.1256. Found: 234.1251.

5-Benzyl-2,2-dimethyl-5-phenethyl-1,3-dioxane-4,6-dione (123): 2,2-Dimethyl-5-phenethyl-1,3-dioxane-4,6-dione²⁹ was alkylated with benzyl bromide according to Procedure B. Purification by recrystallization from MeOH provided a crystalline solid in 22% yield (3 steps from Meldrum's acid); M.p. 117.0-118.0 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 7.30-7.15 (m, 10H), 3.33 (s, 2H), 2.59-2.38 (m, 4H), 1.58 (s, 3H), 0.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.8, 139.6, 135.3, 130.3, 128.9, 128.6, 128.3, 127.8, 126.5, 106.0, 57.6, 43.8, 43.1, 31.8, 29.5, 28.8; HRMS(EI) m/z calcd for $C_{18}H_{16}O_3$ ($M^+ - C_3H_6O$): 280.1099. Found: 280.1088.

2-Benzyl-1,2,3,4-tetrahydro-1-naphthalenone³³ (124): Obtained as the exclusive isomer in 75% yield from **123** using Procedure D in 45 min. Purified by flash chromatography (1:1 CH_2Cl_2 :hexanes) to afford a fine white powder. M.p. 50-51 °C (CH_2Cl_2 /hexanes). Lit. 53-54 °C (petroleum ether); 1H NMR ($CDCl_3$, 300 MHz) δ 8.05 (d, $J = 7.8$ Hz, 1H), 7.45 (dt, $J = 7.1, 1.2$ Hz, 1H), 7.32-7.19 (m, 7H), 3.48 (dd, $J = 13.4, 3.7$ Hz, 1H), 2.94-2.89 (m, 2H), 2.74-2.59 (m, 1H), 2.62 (dd, $J = 13.4, 9.6$ Hz, 1H), 2.09 (dq, $J = 13.4, 4.4$ Hz, 1H), 1.84-1.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 199.4, 144.0, 140.0, 133.3, 132.5, 129.3, 128.7, 128.4, 127.5, 126.6, 126.1, 49.5, 35.7, 28.6, 27.6; HRMS(EI) m/z calcd for $C_{17}H_{16}O$ (M^+): 236.1201. Found: 236.1200.

5-Benzyl-2,2-dimethyl-5-(3-phenylpropyl)-1,3-dioxane-4,6-dione (125): Meldrum's acid was coupled with cinnamic acid using the method of Tsukamoto.²⁹ The resulting intermediate was hydrogenated over 5% Pd/C, then alkylated with benzyl bromide according to Procedure B, and purified by recrystallization from MeOH to afford a crystalline solid in 25% yield (3 steps); M.p. 126-127 °C (MeOH); 1H NMR ($CDCl_3$, 300 MHz) δ 7.29-7.11 (m, 10H), 3.29 (s, 2H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.20-2.15 (m, 2H), 1.65-1.54 (m, 2H), 1.51 (s, 3H), 0.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.9, 140.7, 130.3, 128.9, 128.5, 128.3, 127.8, 126.1, 105.9, 57.6, 43.8, 40.8, 35.5, 29.5, 28.9, 27.0; HRMS(EI) m/z calcd for $C_{19}H_{18}O_3$ ($M^+ - C_3H_6O$): 294.1256. Found: 294.1249.

6-Benzyl-6,7,8,9-tetrahydro-5H-benzo[a]cyclohepten-5-one (126): Obtained as the exclusive isomer in 77% yield from **125** using Procedure D in 45 min. Purified by flash chromatography (9:1 pentane:Et₂O) to afford a clear, colorless oil. 1H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.42 (d, $J = 7.6$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.29-7.01 (m, 5H), 3.30 (dd, $J = 17.2,$

7.9 Hz, 1H), 2.78 (dd, $J = 17.2, 3.9$ Hz, 1H), 2.71-2.62 (m, 3H), 2.05-1.93 (m, 1H), 1.74 (quint., $J = 7.8$ Hz, 2H), 1.55-1.45 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 208.8, 153.7, 142.1, 136.8, 134.7, 128.4, 128.3, 127.3, 126.5, 125.8, 123.9, 47.3, 36.0, 32.8, 31.1, 29.3; HRMS(EI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ (M^+): 250.1358. Found: 250.1358.

2,2-Dimethyl-5-phenethyl-5-(3-phenylpropyl)-1,3-dioxane-4,6-dione (127): 2,2-Dimethyl-5-phenethyl-1,3-dioxane-4,6-dione²⁹ was alkylated with cinnamyl chloride according to Procedure B, and the resulting intermediate hydrogenated over 5% Pd/C and recrystallized from MeOH to provide a crystalline solid in 72% yield (2 steps); M.p. 94.5-95.5 °C (MeOH); ^1H NMR (CDCl_3 , 300 MHz) δ 7.28-7.09 (m, 10H), 2.62-2.53 (m, 4H), 2.28-2.03 (m, 4H), 1.74 (s, 3H), 1.70 (s, 3H), 1.70-1.56 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.2, 128.6, 128.5, 128.3, 126.1, 105.7, 54.5, 29.8, 27.1; HRMS(EI) m/z calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3$ ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$): 308.1412. Found: 308.1407.

2-(3-Phenylpropyl)-1,2,3,4-tetrahydro-1-naphthalenone (128): Obtained as the exclusive isomer in 76% yield from **127** using Procedure D in 45 min. Purified by flash chromatography (9:1 pentane:Et₂O) to afford a clear colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.02 (d, $J = 7.8$ Hz, 1H), 7.44 (dt, $J = 7.5, 1.3$ Hz, 1H), 7.31-7.16 (m, 7H), 2.98-2.95 (m, 2H), 2.66 (dt, $J = 7.7, 2.4$ Hz, 2H), 2.53-2.44 (m, 1H), 2.22 (dq, $J = 13.3, 4.6$ Hz, 1H), 2.06-1.81 (m, 2H), 1.79-1.67 (m, 2H), 1.61-1.49 (m, 1H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 200.2, 143.9, 142.4, 133.1, 132.5, 128.6, 128.4, 128.3, 127.4, 126.5, 125.7, 47.4, 36.1, 29.2, 28.9, 28.3, 28.2; HRMS(EI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{O}$ (M^+): 264.1514. Found: 264.1509.

5-(1,2-Diphenylethyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (129): Phenyl Meldrum's alkylidene³ was prepared by the conjugate addition of phenylmagnesium bromide to 5-methoxymethylene Meldrum's acid³⁴ according to Procedure C, followed by acid hydrolysis with 10% HCl for 30 minutes. After standard workup the phenyl Meldrum's alkylidene was acquired as a pale yellow solid in quantitative yield. This was reacted with benzylmagnesium chloride (Procedure C) to produce the desired target material, which was purified by flash chromatography (1:1 hexanes: CH_2Cl_2) to afford a colorless oil in 82% yield. ^1H NMR (CDCl_3 , 300 MHz) δ 7.39-7.20 (m, 10H), 4.10-4.03 (m, 1H), 3.70 (t, $J = 12.4$ Hz, 1H), 3.53 (d, $J = 2.8$ Hz, 1H), 3.23 (dd, $J = 13.7, 5.7$ Hz, 1H), 1.52 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 166.0, 164.5, 139.5, 139.0, 129.3, 128.9, 128.7, 127.8, 126.7, 105.3, 48.4, 47.7, 38.1, 28.0; HRMS(EI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3$ ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$): 266.0943. Found: 266.0933.

3-Phenyl-1,2,3,4-tetrahydro-1-naphthalenone (130): Obtained as the exclusive isomer in 51% yield from **129** using Procedure D with slow addition of substrate by syringe pump over 8 h, followed by an additional one hour of stirring at 100 °C. Purified by flash chromatography (1:1 hexanes:CH₂Cl₂) to afford a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.39-7.24 (m, 7H), 3.51-3.40 (m, 1H), 3.21-3.17 (m, 2H), 2.97 (dd, *J* = 16.7, 3.5 Hz, 1H), 2.83 (dd, *J* = 16.6, 12.9 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 197.8, 143.4, 133.8, 132.1, 128.8, 127.2, 127.0, 126.9, 126.7, 45.9, 41.1, 37.7; HRMS(EI) *m/z* calcd for C₁₆H₁₄O (M⁺): 222.1045. Found: 222.1044.

5-(1,3-Diphenylpropyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (131): Cinnamaldehyde was condensed with Meldrum's acid using the method of Bigi⁹, and the resulting alkylidene reacted with phenylmagnesium bromide according to Procedure C. The resulting product was hydrogenated over 5% Pd/C to afford the target material as a solid in 56% yield (3 steps from Meldrum's acid) after recrystallization from MeOH. M.p. 72.5-73.5 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.35-7.12 (m, 10H), 3.80-3.74 (m, 1H), 3.67 (d, *J* = 3.2 Hz, 1H), 2.73-2.51 (m, 3H), 2.36-2.24 (m, 1H), 1.59 (s, 3H), 1.11 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.5, 164.6, 141.3, 139.0, 129.1, 128.8, 128.4, 127.8, 126.0, 105.4, 51.4, 45.5, 34.3, 34.1, 28.3, 28.0; HRMS(EI) *m/z* calcd for C₂₁H₂₂O₄ (M⁺): 338.1518. Found: 338.1519.

7-Phenyl-6,7,8,9-tetrahydro-5H-benzo[a]cyclohepten-5-one (132): Obtained as the exclusive isomer in 42% yield from **131** using Procedure D with slow addition of substrate by syringe pump over 8 h, followed by an additional one hour of stirring at 100 °C. Purified by flash chromatography (1:1 hexanes:CH₂Cl₂) to afford a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.31-7.17 (m, 5H), 3.40-3.34 (m, 1H), 2.89 (dd, *J* = 19.0, 7.5 Hz, 1H), 2.75-2.68 (m, 2H), 2.43 (dd, *J* = 19.0, 3.3 Hz, 1H), 2.32-2.20 (m, 1H), 1.86-1.74 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 158.5, 141.4, 136.8, 134.7, 128.5, 128.3, 127.6, 126.1, 125.5, 123.6, 43.0, 37.8, 37.7, 33.9; HRMS(EI) *m/z* calcd for C₁₇H₁₆O (M⁺): 236.1201. Found: 236.1194.

5-(1-Benzyl-3-phenylpropyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (133): Cinnamaldehyde was condensed with Meldrum's acid⁹, and the resulting alkylidene reacted with benzylmagnesium chloride according to Procedure C. The resulting product was hydrogenated over 5% Pd/C to afford the target material as a solid in 65% yield (3 steps from Meldrum's acid) after recrystallization from MeOH. M.p. 83.0-84.0 °C (MeOH); ¹H NMR (CDCl₃, 300 MHz) δ 7.31-7.14 (m, 10H), 3.29 (d, *J* = 2.4 Hz, 1H), 2.98

(dd, $J = 8.1, 2.3$ Hz, 2H), 2.87-2.74 (m, 2H), 2.65-2.55 (m, 1H), 1.98-1.84 (m, 2H), 1.66 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.5, 164.7, 141.5, 139.6, 129.2, 128.7, 128.5, 128.4, 126.7, 126.0, 104.6, 47.4, 40.6, 37.4, 34.3, 32.7, 28.2, 26.7; HRMS(EI) m/z calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3$ ($\text{M}^+ - \text{C}_3\text{H}_6\text{O}$): 294.1256. Found: 294.1260.

3-Phenethyl-1,2,3,4-tetrahydro-1-naphthalenone (134): Obtained as the exclusive isomer in 59% yield from **133** using Procedure D with slow addition of substrate by syringe pump over 8 h, followed by an additional one hour of stirring at 100 °C. Purified by flash chromatography (1:1 hexanes: CH_2Cl_2) to afford a colorless oil. ^1H NMR (CDCl_3 , 300 MHz) δ 8.02 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.32-7.18 (m, 7H), 3.05 (d, $J = 14.0$ Hz, 1H), 2.86-2.79 (m, 1H), 2.72 (t, $J = 7.9$ Hz, 2H), 2.37 (dd, $J = 16.2, 11.9$ Hz, 1H), 2.27-2.19 (m, 1H), 1.78 (quintet, $J = 7.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 198.2, 143.5, 141.7, 133.5, 132.3, 128.9, 128.4, 128.3, 126.9, 126.7, 125.9, 45.2, 37.4, 36.1, 34.7, 32.8; HRMS(EI) m/z calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ (M^+): 250.1358. Found: 250.1366.

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