Synlett Supporting Information:
Superacid Promoted Dual C-C Bond Formation by Friedel-Crafts Alkylation and Acylation of Ethyl Cinnamates: Synthesis of Indanones
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Spectral data for all new compounds S2-S11
Experimental Section:

**General:** IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. $^1$H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl$_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ$_H$ = 0.00 ppm) or CHCl$_3$ (δ$_H$ = 7.25 ppm). $^{13}$C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl$_3$; chemical shifts (δ ppm) are reported relative to CHCl$_3$ [δ$_C$ = 77.00 ppm (central line of triplet)]. In the $^{13}$C NMR, the nature of carbons (C, CH, CH$_2$ and CH$_3$) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH$_2$) and q = quartet (for CH$_3$). In the $^1$H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by $^1$H, $^{13}$C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded using Micromass Q-TOF micro mass spectrometer using electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme’s silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

**GP-1 (General Procedure for Friedel-Crafts Alkylation and Acylation of Ethyl Cinnamates):** To an oven dried Schlenk tube under nitrogen atmosphere, were added ester 1 (100 mg, 0.42–0.57 mmol), arene 2 (in case of benzene, toluene and xylene 12 equivalents and for other electron rich arenes 1.5 equivalents were used for 1 equivalent of the ester 1) and DCE (2 mL), followed by the addition of triflic acid [3 equiv (i.e 1.26–1.71 mmol)]. The resultant reaction mixture was stirred at 80 °C for 12–24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO$_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanone 3 (54–92%).

Compound 1a is commercially available, Compounds 1b, $^1$ 1c, $^2$ 1d, $^3$ 1e, $^4$ 1f, $^5$ 1g, $^6$ 3aa, $^7$ 3ab, $^8$ 3ac, $^9$ 3ba, $^{10}$ 3bc $^{11}$ and 3ca $^{12}$ are known in literature.

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Procedure for Meyers Addition on Ethyl Cinnamate 1c:

**ethyl 3-(3,4-dimethoxyphenyl)-3-phenylbutanoate hydrate (4c):** To an oven dried Schlenk tube under nitrogen atmosphere, were added ester 1c (100 mg, 0.52 mmol), varatrole 2c (108.8 mg, 0.78 mmol) and FeCl₃ (52.2 mg, 0.36 mmol), followed by addition of dry DCM (4 mL). The resulted reaction mixture was stirred at RT for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished the arylated ester 4c (120 mg, 69%) as pale yellow oil. 

[TLC control Rₚ(1c) = 0.80, Rₚ(4c) = 0.30, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νₘₐₓ=2975, 2937, 1730, 1595, 1457, 1409, 1370, 1329, 1255, 1149, 1073, 1029; 954, 853, 766, 701, 660, 596 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ = 7.32–7.22 (m, 2H, ArH), 7.23–7.10 (m, 3H, ArH), 6.79 (d, 1H, J=8.3 Hz, ArH), 3.88 (q, 2H, J=7.3 Hz, OC₂H₃), 3.85 (s, 3H, ArOCH₃), 3.75 (s, 3H, ArOCH₃), 3.10 (s, 2H, CH₂COOEt), 1.86 (s, 3H, ArC(CH₂)CH₃), 0.99 (t, 3H, J=7.3 Hz, OCH₂CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 171.3 (s, C=O), 148.5 (s, ArC), 148.3 (s, ArC), 147.2 (s, ArC), 140.8 (s, ArC), 127.9 (d, 2C, ArCH), 126.9 (d, 2C, ArCH), 126.0 (d, ArCH), 119.0 (d, ArCH), 111.1 (d, ArCH), 110.3 (d, ArCH), 60.0 (t, OCH₂CH₃), 55.8 (q, ArOCH₃), 55.7 (q, ArOCH₃), 46.7 (t, CH₂COOEt), 45.1 [s, Ar(CH₂)CH₃], 28.4 (q, Ar(CH₂)CH₃), 13.9 [q, OCH₂CH₃] ppm. HR-MS (APCI+) m/z calculated for [C₂₀H₂₄O₄]⁺=[M]+: 328.1669; found: 328.1664.

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3-(4-chlorophenyl)-3-methylindan-1-one (3f): GP-1 was carried out with ester 1d (100 mg, 0.44 mmol), benzene 2a (416.6 mg, 5.34 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished indanone 3f (86 mg, 75%) as colorless oil. [TLC control Rf(1d)=0.80, Rf(3f)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}}=2966, 2930, 1710, 1491, 1462, 1288, 1234, 1151, 1093, 1012, 828, 762, 674, 582 \) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): \( \delta=7.78 \) (d, 1H, \( J=7.3 \) Hz, ArH), 7.60 (dd, 1H, \( J=7.8 \) and 7.3 Hz, ArH), 7.43 (dd, 1H, \( J=7.8 \) and 7.3 Hz, ArH), 7.25 (d, 1H, \( J=7.8 \) Hz, ArH), 7.24 (ddd, 2H, \( J=8.8, 2.4 \) and 2.4 Hz, ArH), 7.10 (ddd, 2H, \( J=8.8, 2.4 \) and 2.4 Hz, ArH), 2.91 (d, 1H, \( J=19.1 \) Hz, \( CH_aH_bCO \)), 2.88 (d, 1H, \( J=19.1 \) Hz, \( CH_aH_bCO \)), 1.81 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): \( \delta=205.3 \) (s, C=O), 162.3 (s, ArC), 145.8 (s, ArC), 135.6 (s, ArC), 135.4 (d, ArCH), 132.3 (s, ArC), 128.5 (d, 2C, ArCH), 128.0 (d, ArCH), 127.7 (d, 2C, ArCH), 125.4 (d, ArCH), 123.4 (d, ArCH), 55.5 (t, CH₂CO), 45.6 [s, Ar-C(CH₂CO)CH₃] ppm. HR-MS (APCI+) m/z calculated for \([C_{16}H_{14}ClO]^+=[M+H]^+\): 257.0728; found: 257.0724.

3-(4-chlorophenyl)-3,6-dimethylindan-1-one (3g): GP-1 was carried out with ester 1d (100 mg, 0.44 mmol), toluene 2b (492.0 mg, 5.34 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished indanone 3g (100 mg, 83%) as colorless viscous liquid. [TLC control Rf(1d)=0.80, Rf(3g)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): \( \nu_{\text{max}}=2964, 2851, 1705, 1581, 1488, 1399, 1282, 1244, 1161, 1093, 826, 724, 665, 588 \) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): \( \delta=7.57 \) (s, 1H, ArH),...
7.42 (d, 1H, J=7.8 Hz, ArH), 7.22 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 7.14 (d, 1H, J=7.8 Hz, ArH), 7.10 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 2.89 (d, 1H, J=19.1 Hz, CH₃H₃CO), 2.87 (d, 1H, J=19.1 Hz, CH₂H₂CO), 2.42 (s, 3H, ArCH₃), 1.78 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=205.4 (s, C=O), 159.7 (s, ArC), 146.1 (s, ArC), 138.0 (s, ArC), 136.6 (d, ArCH), 135.9 (s, ArC), 132.2 (s, ArC), 128.5 (d, 2C, ArCH), 127.6 (d, 2C, ArCH), 125.1 (d, ArCH), 123.3 (d, ArCH), 55.8 (t, CH₂CO), 45.3 [s, Ar-C(CH₂CO)CH₃], 28.3 [q, Ar-C(CH₂CO)CH₃], 21.1 (q, ArCH₃) ppm.

HR-MS (APCI+) m/z calculated for [C₁₇H₁₆ClO]⁺=[M+H]⁺: 271.0884; found: 271.0880.

5,6-dimethoxy-3-methyl-3-phenylindan-1-one (3h): GP-1 was carried out with ester 1c (100 mg, 0.52 mmol), veratrole 2c (108.9 mg, 0.79 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.57 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 90:10) furnished indanone 3h (125 mg, 84%) as colorless viscous liquid. [TLC control Rf(2c)=0.80, Rf(3h)=0.40, (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax=2962, 2930, 2836, 1696, 1592, 1496, 1442, 1295, 1212, 1125, 1029, 821, 701 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.36–7.28 (m, 2H, ArH), 7.27–7.18 (m, 4H, ArH), 6.65 (s, 1H, ArH), 3.96 (s, 3H, ArOCH₃), 3.89 (s, 3H, ArOCH₃), 2.93 (d, 1H, J=19.1 Hz, CH₃H₃CO), 2.89 (d, 1H, J=19.1 Hz, CH₂H₂CO), 1.85 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=204.3 (s, C=O), 158.1 (s, ArC), 149.7 (s, ArC), 147.3 (s, ArC), 128.8 (s, ArC), 128.5 (d, 2C, ArCH), 126.3 (d, ArCH), 126.1 (d, 2C, ArCH), 106.1 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, ArOCH₃), 56.1 (q, ArOCH₃), 55.9 (t, CH₂CO), 45.6 [s, Ar-C(CH₂CO)CH₃], 27.9 [q, Ar-C(CH₂CO)CH₃] ppm. HR-MS (APCI+) m/z calculated for [C₁₈H₁₉O₃]⁺=[M+H]⁺: 283.1329; found: 283.1324.

3-(4-chlorophenyl)-5,6-dimethoxy-3-methylindan-1-one (3i): GP-1 was carried out with ester 1d (100 mg, 0.44 mmol), veratrole 2c (92.1 mg, 0.67 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.33 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Progress of the
reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished indanone 3i (125 mg, 88%) as brown viscous liquid. [TLC control \( R_f(1d) = 0.8, R_f(3i) = 0.30 \), (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR–ATR, 4000–600 cm⁻¹): \( \nu_{max} = 2966, 2930, 1710, 1602, 1491, 1462, 1234, 1093, 1011, 828, 761 \) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): \( \delta = 7.21 \) (ddd, 2H, \( J = 8.8, 2.4 \) and \( 2.4 \) Hz, ArH), 7.16 (s, 1H, ArH), 7.08 (ddd, 2H, \( J = 8.8, 2.4 \) and \( 2.4 \) Hz, ArH), 6.56 (s, 1H, ArH), 3.90 (s, 3H, ArOCH₃), 3.84 (s, 3H, ArOCH₃), 2.81 (d, 1H, \( J = 19.1 \) Hz, \( CH_aH_bCO \)), 2.80 (d, 1H, \( J = 19.1 \) Hz, \( CH_aH_bCO \)), 1.77 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz): \( \delta = 203.7 \) (s, C=O), 157.5 (s, ArC), 155.9 (s, ArC), 149.8 (s, ArC), 145.9 (s, ArC), 132.2 (s, ArC), 128.7 (s, ArC), 128.5 (d, 2C, ArCH), 127.6 (d, 2C, ArCH), 105.8 (d, ArCH), 103.5 (d, ArCH), 56.2 (q, ArOCH₃), 56.1 (q, ArOCH₃), 55.7 (t, \( CH_2CH_2CH_3 \)) ppm. HR-MS (APCI+) m/z calculated for \([C_{18}H_{18}ClO_3]^+ = [M+H]^+\): 317.0939; found: 317.0946.

3-ethyl-5,6-dimethoxy-3-phenylindan-1-one (3j): GP-1 was carried out with ester 1e (100 mg, 0.49 mmol), veratrole 2c (92.1 mg, 0.67 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.46 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished indanone 3j (105 mg, 72%) as pale yellow viscous liquid. [TLC control \( R_f(1e) = 0.80, R_f(3j) = 0.30 \), (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR–ATR, 4000–600 cm⁻¹): \( \nu_{max} = 2960, 2921, 2851, 1696, 1592, 1496, 1462, 1302, 1276, 1213, 1039, 861, 766, 701 \) cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): \( \delta = 7.33–7.24 \) (m, 2H, ArH), 7.24–7.14 (m, 4H, ArH), 6.62 (s, 1H, ArH), 3.92 (s, 3H, ArOCH₃), 3.86 (s, 3H, ArOCH₃), 2.86 (d, 1H, \( J = 19.1 \) Hz, \( CH_aH_bCO \)), 2.82 (d, 1H, \( J = 19.1 \) Hz, \( CH_aH_bCO \)), 2.42–2.26 (m, 1H, \( CH_aH_bCH_3 \)), 2.24–2.08 (m, 1H, \( CH_aH_bCH_3 \)), 0.73 (t, 3H, \( J = 7.3 \) Hz, \( CH_2CH_3 \)) ppm. ¹³C NMR (CDCl₃, 100 MHz): \( \delta = 204.4 \) (s, C=O), 155.6 (s, ArC), 155.5 (s, ArC), 149.6 (s, ArC), 147.2 (s, ArC), 130.2 (s, ArC), 128.5 (d, 2C, ArCH), 126.4 (d, 2C, ArCH), 126.3 (d, ArCH), 106.6 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, ArOCH₃), 56.1 (q, ArOCH₃), 52.5 (t, \( CH_2CO \)), 49.8 [s, Ar-C(CH₂CO)CH₂CH₃], 31.8 (t, \( CH_2CH_3 \)), 9.1 (q, \( CH_2CH_3 \)) ppm. HR-MS (APCI+) m/z calculated for \([C_{19}H_{21}O_3]^+ = [M+H]^+\): 297.1485; found: 297.1501.
3-(4-chlorophenyl)-3-ethyl-5,6-dimethoxyindan-1-one (3k): GP-1 was carried out with ester 1f (100 mg, 0.42 mmol), veratrole 2c (86.7 mg, 0.63 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.25 mmol). The resulted reaction mixture was stirred at 80 °C for 12 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished the indanone 3k (101 mg, 73%) as pale brown viscous liquid. [TLC control Rf(1f)=0.80, Rf(3k)=0.30, (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR–ATR, 4000–600 cm⁻¹): νmax=2964, 2922, 2851, 1698, 1592, 1498, 1464, 1302, 1278, 1214, 1094, 1040, 826, 802 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.24 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 7.18 (s, 1H, ArH) 7.12 (ddd, 2H, J=8.8, 2.4 and 2.4 Hz, ArH), 6.57 (s, 1H, ArH), 5.92 (s, 3H, ArOCH₃), 6.86 (s, 3H, ArOCH₃), 2.84 (d, 1H, J=19.1 Hz, CHaHbCO), 2.75 (d, 1H, J=19.1 Hz, CHaHbCO), 2.38–2.22 (m, 1H, CHaHbCH₃), 2.20–2.05 (m, 1H, CHaHbCH₃), 0.71 (t, 3H, J=7.3 Hz, ArC-CH₃) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=203.9 (s, C=O), 155.7 (s, ArC), 155.0 (s, ArC), 149.7 (s, ArC), 145.8 (s, ArC), 132.1 (s, ArC), 130.1 (s, ArC), 128.6 (d, 2C, ArCH), 127.9 (d, 2C, ArCH), 106.3 (d, ArCH), 103.5 (d, ArCH), 56.3 (q, ArOCH₃), 56.1 (q, ArOCH₃), 52.3 (t, CH₂CO), 49.4 [s, Ar-C(Et)CO], 31.7 (t, CH₂CH₃), 9.1 (q, CH₂CH₃) ppm. HR-MS (APCI+) m/z calculated for [C₁₉H₂₀ClO₃]+=[M+H]+: 331.1095; found: 331.1099.

3-(4-bromo-2-methoxyphenyl)indan-1-one (3l): GP-1 was carried out with ester 1a (100 mg, 0.57 mmol), 3-bromoaanisole 2d (159.2 mg, 0.85 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.70 mmol). The resultant reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 85:15) furnished the indanone 3l (111.3 mg, 54%) as pale yellow
viscous liquid. [TLC control $R_f(\text{1a})=0.70$, $R_f(\text{3l})=0.35$, (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{\text{max}}=2938, 1710, 1603, 1589, 1488, 1462, 1397, 1243, 1028, 840, 761$ cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta=7.78$ (d, 1H, $J=7.3$ Hz, ArH), 7.55 (dd, 1H, $J=7.8$ and 7.3 Hz, ArH), 7.39 (dd, 1H, $J=7.8$ and 7.3 Hz, ArH), 7.26 (d, 1H, $J=7.8$ Hz, ArH), 7.00 (s, 1H, ArH), 6.99 (d, 1H, $J=8.3$ Hz, ArH), 6.79 (d, 1H, $J=8.3$ Hz, ArH), 4.81 (dd, 1H, $J=7.8$ and 3.4 Hz, ArCHCH$_2$), 3.73 (s, 3H, ArOCH$_3$), 3.14 (dd, 1H, $J=19.1$ and 7.8 Hz, ArCHCH$_2$H$_6$), 2.61 (dd, 1H, $J=19.1$ and 3.4 Hz, ArCHCH$_2$H$_6$) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta=206.3$ (s, C=O), 157.8 (s, ArC), 157.1 (s, ArC), 137.0 (s, ArC), 134.8 (d, ArCH), 130.7 (s, ArC), 129.5 (d, ArCH), 127.6 (d, ArCH), 126.4 (d, ArCH), 123.6 (d, ArCH), 123.3 (d, ArCH), 121.2 (s, ArC), 114.4 (d, ArCH), 55.6 (q, ArOCH$_3$), 44.9 (t, ArCHCH$_2$), 38.6 (d, ArCHCH$_2$) ppm. HR-MS (APCI+) m/z calculated for $[C_{16}H_{14}BrO_2]^+=[M+H]^+$: 317.0172; found: 317.0186.

3-(2-bromo-4-methoxyphenyl)-3-methylindan-1-one (3m): GP-1 was carried out with ester $\text{1c}$ (100 mg, 0.52 mmol), 3-bromoanisole $\text{2d}$ (147.7 mg, 0.78 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.57 mmol). The resulted reaction mixture was stirred at 80 °C for 24 hrs. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO$_3$ and extracted with DCM (3 $\times$ 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished indanone 3m (160.0 mg, 92%) as white solid, recrystallized the solid with dichloromethane/hexane, m. p. 120–124 °C. [TLC control $R_f(\text{1c})=0.80$, $R_f(\text{3m})=0.40$, (petroleum ether/ethyl acetate 85:15, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{\text{max}}=2965, 2934, 1711, 1602, 1486, 1462, 1392, 1287, 1237, 1157, 1068, 1026, 858, 758, 583$ cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta=7.74$ (d, 1H, $J=7.3$ Hz, ArH), 7.50 (dd, 1H, $J=7.8$ and 7.3 Hz, ArH), 7.35 (dd, 1H, $J=7.8$ and 7.8 Hz, ArH), 7.27 (d, 1H, $J=8.3$ Hz, ArH), 7.13 (d, 1H, $J=7.8$ Hz, ArH), 7.08 (dd, 1H, $J=8.3$ and 1.9 Hz, ArH), 6.88 (d, 1H, $J=1.9$ Hz, ArH), 3.40 (s, 3H, ArOCH$_3$), 3.11 (d, 1H, $J=19.1$ Hz, CH$_2$H$_6$CO), 2.63 (d, 1H, $J=19.1$ Hz, CH$_2$H$_6$CO), 1.71 [s, 3H, ArC(CH$_2$CO)CH$_3$] ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta=206.3$ (s, C=O), 162.4 (s, ArC), 157.9 (s, ArC), 157.8 (s, ArC), 134.5 (d, ArCH), 133.3 (s, ArC), 129.2 (d, ArCH), 127.2 (d, ArCH), 124.2 (d, ArCH), 123.2 (d, ArCH), 123.0 (d, ArCH), 121.5 (s, ArC), 115.3 (d, ArCH), 55.2 (q, ArOCH$_3$), 44.1 [s, ArC(CH$_2$CO)CH$_3$] ppm. HR-MS (APCI+) m/z calculated for $[C_{17}H_{16}BrO_2]^+=[M+H]^+$: 331.0328; found: 331.0343.
6-methyl-3-phenylindan-1-one (3n) and 3-(4-methylphenyl)indan-1-one (5n): GP-1 was carried out, to an oven dried Schlenk tube under nitrogen atmosphere, were added ester 2b (100 mg, 0.57 mmol), toluene (626.5 mg, 6.81 mmol) and DCE (2 mL), followed by the addition of triflic acid (0.15 mL, 1.70 mmol). The resultant reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aq. NaHCO₃ and extracted with DCM (3 × 20 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification of the residue on silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished as an inseparable mixture of indanones 3n & 5n (114.8 mg, 91%) in 3:1 ratio as a pale yellow viscous liquid. [TLC control Rf (2b)=0.65, Rf (3n & 5n)=0.40, (petroleum ether/ethyl acetate 95:5, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹): v_max=2955, 1709, 1602, 1584, 1488, 1454, 1280, 1157, 1046, 822, 758, 699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): (for the major isomer 3n) δ=7.52 (s, 1H, ArH), 7.30 (d, 2H, J=7.8 Hz, ArH), 7.26–7.10 (m, 3H, ArH), 7.07 (d, 1H, J=7.8 Hz, ArH), 6.94 (m, 1H, ArH), 4.44 (dd, 1H, J=7.8 and 3.9 Hz, ArCH₂CH₂), 2.58 (dd, 1H, J=19.1 and 7.8 Hz, ArCHCH₂H₆), 2.58 (dd, 1H, J=19.1 and 3.9 Hz, ArCHCH₂H₆), 2.33 (s, 3H, ArCH₃) ppm.¹³C NMR (CDCl₃, 100 MHz): (for the major isomer 3n) δ=206.1 (s, C=O), 155.4 (s, ArC), 143.9 (s, ArC), 137.8 (d, ArCH), 136.3 (d, ArCH), 129.5 (s, ArC), 128.8 (d, 2C, ArCH), 127.5 (d, 2C, ArCH), 126.8 (d, ArCH), 126.5 (d, ArCH), 123.2 (s, ArC), 47.1 (t, ArCHCH₂), 44.0 (d, ArCHCH₂), 21.1 (q, ArCH₃) ppm. ¹H NMR (CDCl₃, 400 MHz): (for the minor isomer 5n) δ=7.71 (d, 1H, J=7.3 Hz, ArH), 7.60 (dd, 1H, J=7.3 and 2.4 Hz, ArH), 7.47 (ddd, 1H, J=8.8, 7.8 and 1.5 Hz, ArH), 7.38–6.80 (m, 5H, ArH), 4.49 (dd, 1H, J=8.3 and 2.4 Hz, ArCHCH₂), 2.58 (dd, 1H, J=19.1 and 8.3 Hz, ArCHCH₂H₆), 2.51 (dd, 1H, J=19.1 and 2.4 Hz, ArCHCH₂H₆), 2.24 (s, 3H, ArCH₃) ppm.¹³C NMR (CDCl₃, 100 MHz): (for the minor isomer 5n) δ=206.2 (s, C=O), 158.2 (s, ArC), 155.5 (s, ArC), 143.7 (s, ArC), 136.8 (d, ArCH), 136.7 (d, ArCH), 128.4 (d, ArCH), 127.8 (d, ArCH), 126.9 (d, 2C, ArCH), 126.7 (d, 2C, ArCH), 123.4 (s, ArC), 46.9 (t, ArCHCH₂), 43.9 (d, ArCHCH₂), 21.0 (q, ArCH₃) ppm. HR-MS (APCI+) m/z calculated for [C₁₆H₁₅O]+=[M+H]+: 223.1117; found: 223.1108 (for the mixture of 3n and 5n)
3-(4-chlorophenyl)-6-methylindan-1-one (3o) and 6-chloro-3-(4-methylphenyl)indan-1-one (5o): GP-1 was carried out with ester 1b (100 mg, 0.47 mmol), toluene 2b (524.1 mg, 5.70 mmol), DCE (2 mL) and triflic acid (0.1 mL, 1.42 mmol). The resulted reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished an inseparable mixture of indanones 3o & 5o (105 mg, 86%) as brown solid, recrystallized the solid with dichloromethane/hexane, m. p. 110–115 °C (for mixture of 3o and 5o). [TLC control Rf(1b)=0.80, Rf(3o)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹, for mixture of 3o and 5o): νmax=2921, 2854, 1707, 1611, 1487, 1405, 1278, 1242, 1156, 1089, 1048, 935, 822, 783, 695 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz, Peaks due to major isomer 3o): δ=7.48 (s, 1H, ArH), 7.28 (d, 1H, J=7.8 Hz, ArH), 7.14 (ddd, 2H, J=8.3, 2.4 and 2.4 Hz, ArH), 7.01 (d, 1H, J=7.8 Hz, ArH), 6.93 (ddd, 2H, J=8.3, 2.4 and 2.4 Hz, ArH), 4.39 (dd, 1H, J=7.8 and 3.4 Hz, CHCH₂CO), 3.09 (dd, 1H, J=19.1 and 7.8 Hz, CH₂CH₂H₃CO), 2.48 (dd, 1H, J=19.1 and 3.4 Hz, CH₂CH₂H₃CO), 2.30 (s, 3H, ArCH₃) ppm. ¹³CNMR (CDCl₃, 100 MHz, Peaks due to major isomer 3o): δ=205.6 (s, C=O), 154.7 (s, ArC), 142.4 (s, ArC), 138.1 (s, ArC), 136.4 (d, ArCH), 132.6 (s, ArC), 129.0 (s, ArC), 128.9 (d, 2C, ArCH), 128.8 (d, 2C, ArCH) 126.3 (d, ArCH), 123.3 (d, ArCH), 47.0 (t, CH₂CH₂CO), 43.4 (d, CH₂CH₂CO), 21.1 (q, ArCH₃) ppm. ¹H NMR (CDCl₃, 400 MHz, Peaks due to minor isomer 5o): δ=7.56 (d, 1H, J=7.0 Hz, ArH), 7.26 (d, 1H, J=7.0 Hz, ArH), 7.15 (s, 1H, ArH), 7.11 (ddd, 2H, J=8.3, 2.4 and 2.4 Hz, ArH), 6.84 (ddd, 2H, J=8.3, 2.4 and 2.4 Hz, ArH), 4.44 (dd, 1H, J=8.3 and 2.4 Hz, CHCH₂CO), 3.10 (dd, 1H, J=19.1 and 8.3 Hz, CH₂CH₂H₃CO), 2.42 (dd, 1H, J=19.1 and 2.4 Hz, CH₂CH₂H₃CO), 1.90 (s, 3H, ArCH₃) ppm. ¹³CNMR (CDCl₃, 100 MHz, Peaks due to minor isomer 5o): δ=206.1 (s, C=O), 154.9 (s, ArC), 142.1 (s, ArC), 137.0 (s, ArC), 136.8 (d, ArCH), 136.6 (s, ArC), 136.5 (s, ArC), 129.0 (d, 2C, ArCH), 128.6 (d, 2C, ArCH), 128.5 (d, ArCH), 121.0 (d, ArCH), 47.3 (t, CH₂CH₂CO), 43.1 (d, CH₂CH₂CO), 18.3 (q, ArCH₃) ppm. HR-MS (APCI+) m/z calculated for [C₁₆H₁₄ClO]⁺=[M+H]⁺: 257.0728 found: 257.0714 (for mixture of 3o and 5o).

3,6-dimethyl-3-phenylindan-1-one (3p) and 3-methyl-3-(4-methylphenyl)indan-1-one (5p): GP-1 was carried out with ester 1c (100 mg, 0.52 mmol), toluene 2b (581.1 mg, 6.30 mmol),
DCE (2 mL) and triflic acid (0.1 mL, 1.57 mmol). The resulting reaction mixture was stirred at 80 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction is completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 94:6) furnished an inseparable mixture of indanones 3p & 5p (112 mg, 90%). [TLC control Rₛ(1c)=0.80, Rₛ(3p)=0.40, (petroleum ether/ethyl acetate 94:6, UV detection)]. IR (MIR-ATR, 4000–600 cm⁻¹ for mixture of 3p and 5p): νmax=2963, 2920, 2850, 1706, 1614, 1488, 1282, 1243, 1094, 1011, 826, 734, 710, 665 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz Peaks due to major isomer 3p): δ=7.63 (s, 1H, ArH), 7.46 (d, 1H, J=8.3 Hz, ArH), 7.32 (dd, 2H, J=7.8 and 1.5 Hz, ArH), 7.29–7.17 (m, 4H, ArH), 3.02 (d, 1H, J=19.1 Hz, CH₃CO), 2.91 (d, 1H, J=19.1 Hz, CH₃CO), 2.47 (s, 3H, ArCH₃), 1.86 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz Peaks due to major isomer 3p): δ=205.9 (s, C=O), 160.3 (s, ArC), 147.5 (s, ArC), 137.7 (s, ArC), 136.5 (d, ArCH), 135.2 (s, ArC), 129.1 (d, ArCH), 128.4 (d, 2C, ArCH), 126.1 (d, 2C, ArCH), 125.2 (d, ArCH), 123.1 (d, ArCH), 56.0 (t, CH₂CO), 45.6 [s, Ar-C(CH₂CO)CH₃], 28.3 (q, ArCH₃), 21.0 [q, Ar-C(CH₂CO)CH₃] ppm. ¹H NMR (CDCl₃, 400 MHz Peaks due to minor isomer 3p): δ=7.82 (d, 1H, J=7.3 Hz, ArH), 7.63 (ddd, 1H, J=7.3, 7.3 and 1.5 Hz, ArH), 7.45 (ddd, 1H, J=7.3, 7.3 and 1.5 Hz, ArH), 7.32 (d, 1H, J=7.3 Hz, ArH), 7.14 (d, 2H, J=8.8 Hz, ArH), 7.12 (d, 2H, J=8.8 Hz, ArH), 3.00 (d, 1H, J=19.1 Hz, CH₃CO), 2.93 (d, 1H, J=19.1 Hz, CH₃CO), 2.35 (s, 3H, ArCH₃), 1.86 [s, 3H, Ar-C(CH₂CO)CH₃] ppm. ¹³C NMR (CDCl₃, 100 MHz Peaks due to minor isomer 3p): δ=206.0 (s, C=O), 163.0 (s, ArC), 144.3 (s, ArC), 135.9 (d, ArCH), 135.6 (s, ArC), 129.1 (d, ArCH), 127.6 (s, ArC), 126.3 (d, 2C, ArCH), 126.1 (d, 2C, ArCH), 125.5 (d, ArCH), 123.2 (d, ArCH), 55.7 (t, CH₂CO), 45.6 [s, Ar-C(CH₂CO)CH₃], 28.3 (q, ArCH₃), 20.8 [q, Ar-C(CH₂CO)CH₃] ppm. HR-MS (APCI+) m/z calculated for [C₁₇H₁₇O⁺]=[M+H]⁺: 237.1274; found: 237.1273 (for mixture of 3p and 5p).

5-methyl-3',4'-dihydro-2'H-spiro[indene-1,1'-naphthalen]-3(2H)-one (3s): To an oven dried Schlenk tube under nitrogen atmosphere, were added ester 1g (100 mg, 0.52 mmol), toluene 2b (581.1 mg, 6.30 mmol) and DCE (2 mL) followed by the addition of triflic acid (0.1 mL, 1.57 mmol). The resultant reaction mixture was stirred at 50 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5) furnished the spiro-tetracyclic ketone 3s (74.1 mg, 61%) as
Synlett Supporting Information:

Superacid Promoted Dual C-C Bonds Formation by Friedel-Crafts Alkylation and Acylation of Ethyl Cinnamates: Synthesis of Indanones

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$^1$H and $^{13}$C NMR spectrums for all new compounds S2-S22
$^1$H NMR (400 MHz) spectrum of 4c in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 4c in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3f in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3f in CDCl$_3$
$\text{H NMR (400 MHz) spectrum of 3g in CDCl}_3$

$\text{13C NMR (100 MHz) spectrum of 3g in CDCl}_3$
$^1$H NMR (400 MHz) spectrum of 3h in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3h in CDCl$_3$
$^{1}$H NMR (400 MHz) spectrum of $3i$ in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of $3i$ in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3j in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3j in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3k in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3k in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3l in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3l in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3m in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3m in CDCl$_3$
Justification for the structures of 3l and 3m about the formation of initial Friedel-Crafts C-C bond at the ortho-position to the methoxy group:

Usually aromatic methoxy protons in $^1$H-NMR appear around $\delta = 3.8$ ppm. If it is at ortho-position, it is possible to have the methoxy group in the shielding zone of the ortho-substituent. This is in good agreement and reminiscent to those advanced compounds observed in the total synthesis of herbertanes, particularly, the precursors of $\beta$-herbertenol, with the methoxy group at para-position, with respect to the bulky cyclopentane moiety, normally appears at $\delta = 3.8$ ppm whereas, in case of $\alpha$-hebertenol, methoxy group at ortho-position appears at slightly shielding zone at nearly $\delta = 3.72$ ppm. In a convincing way to the above observation, in the present case, the methoxy group appears in the shielding zone (3l: $\delta = 3.73$ ppm, 3m: $\delta = 3.38$ ppm) of indane aromatic ring. Further shielding of methoxy group in case of 3m can be explained based on quaternary carbon atom that may push away the anisyl aromatic moiety in such a way that the methoxy group may slightly experience diamagnetic anisotropy created by indanone moiety. It is also true that in the other systems with para/meta-aromatic methoxy groups the OMe shifts normally appear at around $\delta = 3.8$ ppm and it may be possible to observe further deshielding when the substituent is electron-withdrawing or in extended conjugation.

Furthermore, structures of the 3l and 3m can be confirmed from the correlation spectroscopy as discussed below:

Based on NOESY: We have used this method to recognize the interaction of the methoxy group with methyl group of quaternary center. However, not much spatial interactions can be seen as the system is not rigid enough to restrict the rotation of the anisyl aromatic moiety. Therefore, only slight interaction has been noted at marked in the spectra.

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NOESY (400 MHz) spectrum of 3I in CDCl₃
NOESY (400 MHz) spectrum of 3I in CDCl₃
NOESY (400 MHz) spectrum of 3m in CDCl₃

**Based on HMBC:** This method gave crucial information about the position of methoxy group as the methoxy attached carbon coupled with one ortho-, one meta- protons and not the para-proton, whereas, bromine attached carbon coupled with all three protons (two meta- and one ortho-). Moreover, methoxy group coupled well with methyl (proton) of the quaternary (tertiary) carbon and with two α-hydrogens of indanone as in the spectra.
HMBC (100 MHz) spectrum of 3l in CDCl₃
HMBC (100 MHz) spectrum of 3I in CDCl₃
HMBC (100 MHz) spectrum of 3m in CDCl₃
HMBC (100 MHz) spectrum of 3m in CDCl₃
$^1$H NMR (400 MHz) spectrum of 3o in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3o in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3p in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3p in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3s in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3s in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 3t in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 3t in CDCl$_3$
yellow viscous liquid. [TLC control $R_f(1g)$=0.55, $R_f(3s)$=0.40, (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{max}$=2926, 1711, 1581, 1487, 1448, 1281, 1243, 1160, 1050, 1026, 763, 732 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$=7.58 (s, 1H, ArH), 7.40 (d, 1H, $J$=7.3 Hz, ArH), 7.13 (d, 1H, $J$=7.3 Hz, ArH), 7.11 (d, 1H, $J$=7.8 Hz, ArH), 7.10 (dd, 1H, $J$=7.8 and 7.3 Hz, ArH), 7.00 (dd, 1H, $J$=7.8 and 7.3 Hz, ArH), 6.61 (d, 1H, $J$=7.8 Hz, ArH), 3.05–2.88 (m, 3H, ArCH$_2$CH$_2$CH$_2$ and CH$_2$H$_6$CO), 2.85 (d, 1H, $J$=19.1 Hz, CH$_2$H$_6$CO), 2.42 (s, 3H, ArCH$_3$), 2.16–2.00 (m, 2H, ArCH$_2$CH$_2$CH$_2$), 1.96–1.80 (m, 2H, ArCH$_2$CH$_2$CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$=206.2 (s, C=O), 161.4 (s, ArC), 142.2 (s, ArC), 137.7 (s, ArC), 136.7 (s, ArC), 136.6 (s, ArC), 129.0 (d, ArCH), 128.1 (d, ArCH), 126.4 (d, ArCH), 126.2 (d, ArCH), 125.4 (d, ArCH), 122.9 (d, ArCH), 56.0 (t, CH$_2$CO), 46.3 [s, (CO)CH$_2$CH$_2$CH$_2$], 39.5 (t, ArCH$_2$CH$_2$CH$_2$), 29.8 (t, CH$_2$), 21.1 (q and t, 2C, ArCH$_3$ and CH$_2$) ppm. HR-MS (APCI+) m/z calculated for [C$_{19}$H$_{19}$O]$^+=$[M+H]$^+$: 263.1430; found: 263.1436.

5,6-dimethoxy-3',4'-dihydro-2'H-spiro[indene-1,1'-naphthalen]-3(2H)-one (3t): To an oven dried Schlenk tube under nitrogen atmosphere, were added ester 1g (100 mg, 0.46 mmol), veratrole 2c (96.8 mg, 0.69 mmol) and DCE (2 mL) followed by the addition of triflic acid (0.12 mL, 1.70 mmol). The resultant reaction mixture was stirred at 50 °C for 24 h. Progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was quenched by addition of aqueous NaHCO$_3$ and extracted with DCM (3 × 20 mL). The combined organic layers were washed with saturated NaCl solution, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 80:20) furnished spiro-tetracyclic ketone 3t (98.4 mg, 67%) as pale yellow semi-solid. [TLC control $R_f(1g)$=0.75, $R_f(3s)$=0.40, (petroleum ether/ethyl acetate 75:25, UV detection)]. IR (MIR-ATR, 4000–600 cm$^{-1}$): $\nu_{max}$=2933, 1693, 1592, 1496, 1464, 1453, 1290, 1049, 1025, 803, 729, 701 cm$^{-1}$. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$=7.20 (s, 1H, ArH), 7.12 (d, 1H, $J$=7.3 Hz, ArH), 7.10 (dd, 1H, $J$=7.8 and 7.3 Hz, ArH), 7.01 (dd, 1H, $J$=7.8 and 7.8 Hz, ArH), 6.62 (d, 1H, $J$=7.8 Hz, ArH), 6.58 (s, 1H, ArH), 6.58 (s, 1H, ArH), 3.93 (s, 3H, ArOCH$_3$), 3.83 (s, 3H, ArOCH$_3$), 2.95 (dd, 2H, $J$=11.2 and 5.4 Hz, ArCH$_2$CH$_2$CH$_2$), 2.88 (d, 1H, $J$=19.1 Hz, CH$_2$H$_6$CO), 2.78 (d, 1H, $J$=19.1 Hz, CH$_2$H$_6$CO), 2.16–2.00 (m, 2H, ArCH$_2$CH$_2$CH$_2$), 1.96–1.76 (m, 2H, ArCH$_2$CH$_2$CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$=204.6 (s, C=O), 159.0 (s, ArC), 155.9 (s, ArC), 149.7 (s, ArC), 142.1 (s, ArC), 136.6 (s, ArC), 129.6 (s, ArC), 129.0 (d, ArCH), 128.0 (s, ArC), 126.6 (d, ArCH), 126.3 (d, ArCH), 106.2 (d, ArCH), 103.3 (d, ArCH), 56.3 (q, ArOCH$_3$), 56.1 (q, ArOCH$_3$), 55.9 (t, CH$_2$CO), 46.4 [s, (CO)CH$_2$CH$_2$CH$_2$], 39.2 (t, ArCH$_2$CH$_2$CH$_2$), 29.7 (t, CH$_2$), 21.2 (t, CH$_2$) ppm. HR-MS (APCI+) m/z calculated for [C$_{20}$H$_{21}$O$_3$]$^+=$[M+H]$^+$: 309.1485; found: 309.1463.