Supporting Information:

An Efficient Synthesis of Highly Substituted Indanones and Chalcones Promoted By Superacid

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Spectral data for all new compounds S2-S11
Experimental:

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 ($\delta$ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\text{TMS}}=0.00$ ppm) or CHCl$_3$ ($\delta_{\text{H}}=7.25$ ppm). $^{13}$C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl$_3$; chemical shifts ($\delta$ ppm) are reported relative to CHCl$_3$ [$\delta_{\text{C}}=77.00$ 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, sept = septet, dd = doublet of doublet, 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 on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small scale dry reactions were carried out using Schlenk tubes under inert atmosphere. 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 60 to 80 $^\circ$C was used. Dichloroethane (DCE) was dried over CaH$_2$ and absolute ethanol was purchased from local sources, used as received. 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 preparation of 2,2-dimethyl-3-phenylindan-1-ones 3): In an oven dried Schlenk tube, were added ketone 1 (37.0–59.6 mg, 0.25 mmol), benzaldehyde 2 (53.0–92.5 mg, 0.50 mmol) and dichloroethane (1.5 mL) followed by triflic acid (0.11 mL, 1.25 mmol) at room temperature under nitrogen atmosphere. The reaction mixture stirred at room temperature and was then heated in an oil bath at 50 $^\circ$C for 24 h (80 $^\circ$C for 48 h in case of phenylisopropyl ketone) and monitored by TLC. Then, the mixture was quenched by the addition of aqueous NaHCO$_3$ solution and then extracted with ethyl acetate (3 $\times$ 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na$_2$SO$_4$), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the indanones 3 (50–86%).

GP-2 [General procedure for preparation of (2E)-1,3-diphenylprop-2-en-1-ones (chalcones) 6]: In an oven dried Schlenk tube, were added ketone 5 (60.0–99.5 mg, 0.50 mmol), benzaldehyde 2 (106.0–185.0 mg, 1.00 mmol) and dichloroethane (3.0 mL) followed by triflic acid (0.22 mL, 2.5 mmol) at room temperature under nitrogen atmosphere. The reaction mixture stirred at room temperature and was then heated in an oil bath at 50 $^\circ$C for 24 h and monitored by TLC. Then, the mixture was quenched by the addition of aqueous NaHCO$_3$ solution and then extracted with ethyl acetate (3 $\times$ 15 mL). The organic layer was washed with saturated NaCl solution, dried (Na$_2$SO$_4$), and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the chalcones 6 (79–94%).
The following isopropyl ketones 1a–1d, which have been used as starting materials are reported in literature.\(^1\)

![Diagram of isopropyl ketones 1a–1d]

The following benzaldehydes 2a–2h, which are used as starting materials, are commercially available.

![Diagram of benzaldehydes 2a–2h]

The following isopropyl ketones 6a–6i, which have been prepared are reported in literature.\(^2\)

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2,2-dimethyl-3-phenylindan-1-one (3a): GP-1 was carried out with ketone 1a (37.0 mg, 0.25 mmol), aldehyde 2a (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 80 °C for 48 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 99:1 to 95:5) furnished the indanone 1a (15.2 mg, 50%) as a pale yellow viscous liquid along with the recovery of starting material 1a (18 mg, 49%). [TLC control (petroleum ether/ethyl acetate 97:3), \( R_f(1a)=0.49 \), \( R_f(3a)=0.27 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}}=2922, 1713, 1602, 1494, 1452, 1240, 1212, 1035, 753, 699 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta=7.83 \text{ (d, 1H, } J=7.8 \text{ Hz, Ar-H)}, 7.67 \text{ (ddd, 1H, } J=8.3, 7.8 \text{ and } 1.5 \text{ Hz, Ar-H)}, 7.54 \text{ (d, 1H, } J=7.8 \text{ Hz, Ar-H)}, 7.42 \text{ (ddd, 1H, } J=8.3, 7.8 \text{ and } 1.5 \text{ Hz, Ar-H)}, 7.35 \text{ (dd, 2H, } J=8.3 \text{ and } 7.8 \text{ Hz, Ar-H)}, 7.29 \text{ (tt, 1H, } J=7.8 \text{ and } 1.5 \text{ Hz, Ar-H)}, 7.13 \text{ (dd, 2H, } J=8.3 \text{ and } 1.5 \text{ Hz, Ar-H)}, 3.78 \text{ (s, 1H, CH)}, 1.58 \text{ [s, 3H, C(CH}_3}_2 \text{a]} \text{ and } 0.90 \text{ [s, 3H, C(CH}_3}_2 \text{b]} \text{ ppm}. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta=205.5 \text{ (s, C=O)}, 162.2 \text{ (s, Ar-C)}, 136.7 \text{ (s, Ar-C)}, 135.2 \text{ (d, Ar-CH)}, 135.0 \text{ (s, Ar-C)}, 130.1 \text{ (d, } 2\text{C, } 2\times \text{ Ar-CH)}, 128.4 \text{ (d, } 2\text{C, } 2\times \text{ Ar-CH)}, 127.6 \text{ (d, Ar-CH)}, 127.1 \text{ (d, Ar-CH)}, 123.8 \text{ (d, Ar-CH)}, 123.6 \text{ (d, Ar-CH)}, 67.0 \text{ (d, CH)}, 43.8 \text{ [s, C(CH}_3}_2 \text{]}, 28.5 \text{ [q, C(CH}_3}_2 \text{a]}, 28.4 \text{ [q, C(CH}_3}_2 \text{b]} \text{ ppm. HR-MS (ESI+) m/z calculated for } [\text{C}_{17}{\text{H}}_{17}\text{O}^+]^+=[\text{M+H}]^+: 237.1274; \text{ found 237.1272.}

3-(4-chlorophenyl)-2,2-dimethylindan-1-one (3b): GP-1 was carried out with ketone 1a (37.0 mg, 0.25 mmol), aldehyde 2c (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol),
dichloroethane (1.5 mL) for the formation of indanone at 80 °C for 48 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 99:1 to 95:5) furnished the indanone 3b (17.7 mg, 54%) as a pale yellow viscous liquid along with the recovery of starting material 1a (19 mg, 51%). [TLC control (petroleum ether/ethyl acetate 97:3), \( R_f(1a)=0.49, \ R_f(3b)=0.28, \) UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}}=2943, \ 1714, \ 1604, \ 1493, \ 1443, \ 1375, \ 1099, \ 919, \ 832 \) cm\(^{-1}\). 1H NMR (CDCl\(_3\), 400 MHz): \( \delta=7.81 \) (d, 1H, \( J=8.8 \) Hz, Ar-H), 7.67 (dd, 1H, \( J=8.8 \) and 7.8 Hz, Ar-H), 7.53 (d, 1H, \( J=7.3 \) Hz, Ar-H), 7.42 (dd, 1H, \( J=7.8 \) and 7.3 Hz, Ar-H), 7.32 (d, 2H, \( J=8.3 \) Hz, Ar-H), 7.07 (d, 2H, \( J=8.3 \) Hz, Ar-H), 3.74 (s, 1H, CH), 1.56 \[s, 3H, C(CH\(_3\))\(_2\)\], 0.88 \[s, 3H, C(CH\(_3\))\(_2\)\] ppm. 13C NMR (CDCl\(_3\), 100 MHz): \( \delta=204.9 \) (s, C=O), 162.0 (s, Ar-C), 135.3 (d, Ar-CH), 135.1 (s, Ar-C), 134.7 (s, Ar-C), 133.1 (s, Ar-C), 131.4 (d, 2C, 2 × Ar-CH), 128.6 (d, 2C, 2 × Ar-CH), 127.7 (d, Ar-CH), 123.9 (d, Ar-CH), 123.6 (d, Ar-CH), 66.3 (d, CH), 43.7 \[s, C(CH\(_3\))\(_2\)\], 28.5 \[q, C(CH\(_3\))\(_2\)\], 28.3 \[q, C(CH\(_3\))\(_2\)\] ppm. HR-MS (ESI+) m/z calculated for \([C_{17}H_{16}ClO]^+=[M+H]^+\): 271.0884; found 271.0882.

5,6-dimethoxy-2,2-dimethyl-3-phenylindan-1-one (3c): GP-1 was carried out with ketone 1c (52.0 mg, 0.25 mmol), aldehyde 2a (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone 3c (62.9 mg, 85%) as yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15), \( R_f(1c)=0.45, \ R_f(3c)=0.40, \) UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}}=2964, \ 2928, \ 1697, \ 1591, \ 1498, \ 1465, \ 1453, \ 1303, \ 1264, \ 1220, \ 1109, \ 1018, \ 911, \ 866, \ 728, \ 702 \) cm\(^{-1}\). 1H NMR (CDCl\(_3\), 400 MHz): \( \delta=7.37 \)–7.21 (m, 3H, Ar-H), 7.24 (s, 1H, Ar-H), 7.02 (d, 2H, \( J=7.3 \) Hz, Ar-H), 6.72 (s, 1H, Ar-H), 4.23 (s, 1H, CH), 3.94 (s, 3H, Ar-OCH\(_3\)), 3.84 (s, 3H, Ar-OCH\(_3\)), 1.32 \[s, 3H, C(CH\(_3\))\(_2\)\], 0.88 \[s, 3H, C(CH\(_3\))\(_2\)\] ppm. 13C NMR (CDCl\(_3\), 100 MHz): \( \delta=209.4 \) (s, C=O), 155.7 (s, Ar-C), 149.9 (s, Ar-C), 140.5 (s, Ar-C), 129.2 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 126.9 (d, Ar-CH), 107.8 (d, Ar-CH), 104.4 (d, Ar-CH), 57.3 (d, CH), 56.3 (q, Ar-OCH\(_3\)), 56.1 (q, Ar-OCH\(_3\)), 50.7 \[s, C(CH\(_3\))\(_2\)\], 25.8 \[q, C(CH\(_3\))\(_2\)\], 22.8 \[q, C(CH\(_3\))\(_2\)\] ppm.

3-(4-chlorophenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3d): GP-1 was carried out with ketone 1c (52.0 mg, 0.25 mmol), aldehyde 2c (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25...
mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone 3d (53.7 mg, 65%) as a pale brown solid, recrystallized the solid with dichloromethane/hexane, m. p. 110–112 °C. [TLC control (petroleum ether/ethyl acetate 80:20), \( R_f(3d) = 0.45 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}} = 2964, 2928, 1697, 1590, 1500, 1491, 1464, 1301, 1219, 1112, 1015, 913, 866, 845, 770, 728 \) cm\(^{-1}\).

\( ^1 \)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.27 \) (d, 2H, \( J = 8.3 \) Hz, Ar-H), 7.23 (s, 1H, Ar-H), 6.95 (d, 2H, \( J = 8.3 \) Hz, Ar-H), 6.66 (s, 1H, Ar-H), 4.20 (s, 1H, CH), 3.93 (s, 3H, Ar-OCH\(_3\)), 3.84 (s, 3H, Ar-OCH\(_3\)), 1.31 [s, 3H, C(CH\(_3\))\(_2\)] ppm.

\( ^13 \)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 208.8 \) (s, C=O), 155.9 (s, Ar-C), 150.1 (s, Ar-C), 148.9 (s, Ar-C), 139.1 (s, Ar-C), 132.8 (s, Ar-C), 130.5 (d, 2C, 2 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 107.6 (d, Ar-CH), 104.5 (d, Ar-CH), 56.7 (d, CH), 56.3 (q, Ar-OCH\(_3\)), 56.1 (q, Ar-OCH\(_3\)), 50.6 [s, C(CH\(_3\))\(_2\)], 22.8 [q, C(CH\(_3\))\(_2\)] ppm.

HR-MS (ESI+) m/z calculated for [C\(_{19}\)H\(_{20}\)ClO\(_3\)]\(^+\) = [M+H]\(^+\): 331.1095; found 331.1095.

\( 3-(4\text{-bromophenyl})\)-5,6-dimethoxy-2,2-dimethylindan-1-one (3e): GP-1 was carried out with ketone 1c (52.0 mg, 0.25 mmol), aldehyde 2d (92.5 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone 3e (61.9 mg, 66%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 114–116 °C. [TLC control (petroleum ether/ethyl acetate 80:20), \( R_f(3e) = 0.45 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}} = 2964, 2926, 2867, 1697, 1590, 1500, 1300, 1219, 1112, 1010, 729 \) cm\(^{-1}\). \( ^1 \)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.42 \) (d, 2H, \( J = 8.8 \) Hz, Ar-H), 7.23 (s, 1H, Ar-H), 6.89 (d, 2H, \( J = 8.8 \) Hz, Ar-H), 6.66 (s, 1H, Ar-H), 4.18 (s, 1H, CH), 3.93 (s, 3H, Ar-OCH\(_3\)), 3.84 (s, 3H, Ar-OCH\(_3\)), 1.31 [s, 3H, C(CH\(_3\))\(_2\)], 0.66 [s, 3H, C(CH\(_3\))\(_2\)] ppm. \( ^13 \)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 208.8 \) (s, C=O), 155.9 (s, Ar-C), 150.1 (s, Ar-C), 148.9 (s, Ar-C), 139.1 (s, Ar-C), 132.8 (s, Ar-C), 130.5 (d, 2C, 2 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 107.6 (d, Ar-CH), 104.5 (d, Ar-CH), 56.7 (d, CH), 56.3 (q, Ar-OCH\(_3\)), 56.1 (q, Ar-OCH\(_3\)), 50.6 [s, C(CH\(_3\))\(_2\)], 25.9 [q, C(CH\(_3\))\(_2\)], 22.8 [q, C(CH\(_3\))\(_2\)] ppm. HR-MS (ESI+) m/z calculated for [C\(_{19}\)H\(_{20}\)BrO\(_3\)]\(^+\) = [M+H]\(^+\): 375.0590; found 375.0594.
5,6-dimethoxy-3-(4-methoxyphenyl)-2,2-dimethylindan-1-one (3f): GP-1 was carried out with ketone 1c (52.0 mg, 0.25 mmol), aldehyde 2e (68.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 92:8 to 80:20) furnished the indanone 3f (67.7 mg, 83%) as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20), \( R_f(1c) = 0.45, R_f(3f) = 0.34 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}} = 2963, 2930, 2836, 1695, 1591, 1499, 1464, 1301, 1264, 1218, 1176, 1106, 1018, 911, 726 \) cm\(^{-1}\). 1H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.21 \) (s, 1H, Ar-H), 6.92 (d, 2H, \( J = 8.8 \) Hz, Ar-H), 6.82 (d, 2H, \( J = 8.8 \) Hz, Ar-H), 6.70 (s, 1H, Ar-H), 4.16 (s, 1H, CH), 3.92 (s, 3H, Ar-OC\(_3\)), 3.83 (s, 3H, Ar-OC\(_3\)), 3.77 (s, 3H, Ar-OC\(_3\)), 1.28 \[ s, 3H, \text{C(CH}_3_2a} \], 0.65 \[ s, 3H, \text{C(CH}_3_2b} \] ppm. 13C NMR (CDCl\(_3\), 100 MHz): \( \delta = 209.5 \) (s, C=O), 158.5 (s, Ar-C), 155.7 (s, Ar-C), 149.8 (s, Ar-C), 149.7 (s, Ar-C), 132.4 (s, Ar-C), 130.1 (d, 2C, Ar-CH), 128.1 (s, Ar-C), 113.6 (d, 2C, Ar-CH), 107.7 (d, Ar-CH), 104.3 (d, Ar-CH), 56.5 (d, CH), 56.2 (q, Ar-OCH\(_3\)), 56.1 (q, Ar-OCH\(_3\)), 50.7 [s, C(CH\(_3\)_2ab]], 25.6 [q, C(CH\(_3\)_2a]], 22.8 [q, C(CH\(_3\)_2b]] ppm. HR-MS (ESI+) m/z calculated for \([\text{C}_{20}\text{H}_{23}\text{O}_4]^+ = \text{[M+H]}^+\) : 327.1591; found 327.1591.

3-(3,4-dimethoxyphenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3g): GP-1 was carried out with ketone 1c (52.0 mg, 0.25 mmol), aldehyde 2f (83.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone 3g (69.5 mg, 78%) as a brown solid, recrystallized the solid with dichloromethane/hexane, m. p. 96–98 °C. [TLC control (petroleum ether/ethyl acetate 70:30), \( R_f(1c) = 0.53, R_f(3g) = 0.20 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \nu_{\text{max}} = 2962, 2931, 2867, 2836, 1695, 1590, 1513, 1499, 1463, 1416, 1305, 1265, 1108, 1018, 866, 730, 699 \) cm\(^{-1}\). 1H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.19 \) (s, 1H, Ar-H), 6.77 (d, 1H, \( J = 8.3 \) Hz, Ar-H), 6.69 (s, 1H, Ar-H), 6.55 (br. s, 1H, Ar-H), 6.45 (br. s, 1H, Ar-H), 4.13 (s, 1H, CH), 3.89 (s, 3H, Ar-OCH\(_3\)), 3.81 (s, 3H, Ar-OCH\(_3\)), 3.80 (s, 3H, Ar-OCH\(_3\)), 3.73 (s, 3H, Ar-OCH\(_3\)), 1.26 [s, 3H, C(CH\(_3\)_2ab)], 0.64 [s, 3H, C(CH\(_3\)_2ab)] ppm. 13C NMR (CDCl\(_3\), 100 MHz): \( \delta = 209.3 \) (s, C=O), 155.6 (s, Ar-C), 149.7 (s, Ar-C), 149.4 (s, Ar-C), 148.6 (s, Ar-C), 147.9 (s, Ar-C), 132.7 (s, Ar-C), 128.0 (s, Ar-C), 121.3 (d, Ar-CH), 112.2 (d, Ar-CH), 110.8 (d, Ar-CH), 107.6 (d, Ar-CH), 104.2 (d, Ar-CH), 56.8 (d, CH), 56.1 (q, Ar-OCH\(_3\)), 55.9 (q, Ar-OCH\(_3\)), 55.7 (q, Ar-OCH\(_3\)), 55.6 (q, Ar-OCH\(_3\)), 50.6 [s, C(CH\(_3\)_2)], 25.6 [q, C(CH\(_3\)_2ab)], 22.6 [q, C(CH\(_3\)_2ab)] ppm. HR-MS (ESI+) m/z calculated for \([\text{C}_{21}\text{H}_{25}\text{O}_5]^+ = \text{[M+H]}^+\) : 357.1697; found 357.1696.
4,5,6-trimethoxy-2,2-dimethyl-3-phenylindan-1-one (3i): GP-1 was carried out with ketone 1d (59.5 mg, 0.25 mmol), aldehyde 2a (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethanol acetate, 95:5 to 85:15) furnished the indanone 3i (70.2 mg, 86%) as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), Rf(1d)=0.47, Rf(3i)=0.38, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν max=2966, 2935, 1703, 1602, 1469, 1342, 1313, 1123, 1087, 906, 726 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.50–7.20 (m, 6H, Ar-H), 4.41 (s, 1H, CH), 4.07 (s, 3H, Ar-OCH₃), 4.05 (s, 3H, Ar-OCH₃), 3.52 (s, 3H, Ar-OCH₃), 1.45 [s, 3H, C(CH₃)₂a], 0.87 [s, 3H, C(CH₃)₂b] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=210.1 (s, C=O), 154.8 (d, Ar-CH), 150.5 (d, Ar-CH), 148.7 (d, Ar-CH), 141.6 (d, Ar-CH), 141.3 (d, Ar-CH), 130.6 (d, Ar-CH), 128.1 (d, 3C, Ar-CH), 126.6 (d, 2C, Ar-CH), 100.8 (d, Ar-CH), 60.8 (q, Ar-OCH₃), 60.0 (q, Ar-OCH₃), 56.2 (q, Ar-OCH₃), 55.1 (d, CH), 50.7 [s, C(CH₃)₂a], 28.3 [q, C(CH₃)₂b] ppm. HR-MS (ESI+) m/z calculated for [C₂₀H₂₃O₄]+= [M+H]⁺: 327.1591; found 327.1590.

3-(4-chlorophenyl)-4,5,6-trimethoxy-2,2-dimethylindan-1-one (3j): GP-1 was carried out with ketone 1d (59.5 mg, 0.25 mmol), aldehyde 2c (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethanol acetate, 95:5 to 90:10) furnished the indanone 3j (57.7 mg, 64%) as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), Rf(1d)=0.47, Rf(3j)=0.41, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν max=2967, 2935, 1705, 1600, 1469, 1417, 1343, 1311, 1121, 1013, 912, 848, 770, 728 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.50–6.10 (m, 5H, Ar-H), 4.22 (s, 1H, CH), 3.91 (s, 3H, Ar-OCH₃), 3.89 (s, 3H, Ar-OCH₃), 1.28 [s, 3H, C(CH₃)₂a], 0.70 [s, 3H, C(CH₃)₂b] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=209.6 (s, C=O), 155.0 (s, Ar-C), 148.7 (d, 4C, Ar-CH), 100.9 (d, Ar-CH), 60.9 (q, Ar-OCH₃), 60.1 (q, Ar-OCH₃), 56.2 (q, Ar-OCH₃), 54.4 (d, CH), 50.5 [s, C(CH₃)₂a], 28.1 [q, C(CH₃)₂b], 21.7 [q, C(CH₃)₂b] ppm. HR-MS (ESI+) m/z calculated for [C₂₀H₂₂ClO₄]+= [M+H]⁺: 361.1201; found 361.1196.
4,5,6-trimethoxy-3-(4-methoxyphenyl)-2,2-dimethylindan-1-one (3k): GP-1 was carried out with ketone 1d (59.5 mg, 0.25 mmol), aldehyde 2e (68.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone 3k (67.7 mg, 76%) as a pale brown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), Rf(1d)=0.47, Rf(3k)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax=2964, 2933, 2837, 1704, 1600, 1511, 1467, 1417, 1342, 1310, 1244, 1121, 1033, 731 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.20–6.50 (m, 5H, Ar-H), 4.20 (s, 1H, CH), 3.91 (s, 3H, Ar-OCH₃), 3.89 (s, 3H, Ar-OCH₃), 3.74 (s, 3H, Ar-OCH₃), 3.39 (s, 3H, Ar-OCH₃), 1.27 [s, 3H, C(CH₃)₂a], 0.71 [s, 3H, C(CH₃)₂b] ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=210.2 (s, C=O), 158.2 (s, 2C, Ar-C), 154.8 (s, Ar-C), 150.5 (s, Ar-C), 148.7 (s, Ar-C), 141.5 (s, Ar-C), 133.7 (s, Ar-C), 130.5 (s, Ar-C), 129.3 (d, Ar-CH), 125.0 (d, Ar-CH), 113.4 (d, Ar-CH), 100.8 (d, Ar-CH), 60.8 (q, Ar-OCH₃), 56.2 (q, Ar-OCH₃), 55.1 (q, Ar-OCH₃), 54.4 (d, CH), 50.7 [s, C(CH₃)₂], 28.2 [q, C(CH₃)₂a], 21.7 [q, C(CH₃)₂b] ppm. HR-MS (ESI+) m/z calculated for [C₂₁H₂₅O₅]⁺=[M+H]⁺: 357.1697; found 357.1694.

6-methoxy-2,2-dimethyl-3-phenylindan-1-one (4a) & 4-methoxy-2,2-dimethyl-3-phenylindan-1-one (4a‘): GP-1 was carried out with ketone 1b (44.5 mg, 0.25 mmol), aldehyde 2a (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the inseparable regiosomeric mixture of indanones 4a (42.6 mg, 64%) and 4a‘ (10.6 mg, 16%) as a colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), Rf(1b)=0.50, Rf(4a & 4a‘)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): νmax=2965, 2927, 1711, 1602, 1488, 1465, 1291, 1270, 1241, 1027, 757, 702 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz, peaks due to major isomer 4a): δ=7.35–7.10 (m, 6H, Ar-H), 7.02 (d, 2H, J=7.3 Hz, Ar-H), 4.26 (s, 1H, CH), 3.88 (s, 3H, Ar-OCH₃), 1.35 [s, 3H, C(CH₃)₂a], 0.69 [s, 3H, C(CH₃)₂b] ppm. ¹³C NMR (CDCl₃, 100 MHz, peaks due to major isomer 4a): δ=210.7 (s, C=O), 159.8 (s, Ar-C), 147.1 (s, Ar-C), 140.4 (s, Ar-C), 136.7 (s, Ar-C), 129.2 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 128.7 (d, Ar-CH), 126.9 (d, Ar-CH), 124.3 (d, Ar-CH), 105.1 (d, Ar-CH), 56.8 (d, CH), 55.6 (q, Ar-OCH₃), 51.4 [s, C(CH₃)₂], 25.5 [q, C(CH₃)₂a], 22.8 [q, C(CH₃)₂b] ppm. HR-MS (ESI+) m/z calculated for [C₁₈H₁₉O₂]⁺=[M+H]⁺: 267.1380; found 267.1380.
3-(4-chlorophenyl)-6-methoxy-2,2-dimethylindan-1-one (4b) & 3-(4-chlorophenyl)-4-methoxy-2,2-dimethylindan-1-one (4b'): GP-1 was carried out with ketone 1b (44.5 mg, 0.25 mmol), aldehyde 2c (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the inseparable regioisomeric mixture of indanones 4b (56.2 mg, 68%) and 4b' (14.0 mg, 17%) as a pale yellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 78–81 °C. [TLC control (petroleum ether/ethyl acetate 90:10), \( R_f(1b) = 0.50, R_f(4b \& 4b') = 0.42 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \tilde{\nu}_{\text{max}} = 2963, 2926, 1707, 1599, 1488, 1465, 1270, 1241, 1089, 1013, 796 \text{ cm}^{-1} \). 1H NMR (CDCl\(_3\), 400 MHz, peaks due to major isomer 4b): \( \delta = 7.32 - 7.17 \) (m, 5H, Ar-H), 6.96 (d, 2H, \( J = 8.3 \) Hz, Ar-H), 4.23 (s, 1H, CH), 3.88 (s, 3H, Ar-OCH\(_3\)), 1.34 [s, 3H, C(CH\(_3\))\(_2a\)], 0.69 [s, 3H, C(CH\(_3\))\(_2b\)] ppm. 13C NMR (CDCl\(_3\), 100 MHz, peaks due to major isomer 4b): \( \delta = 210.2 \) (s, C=O), 160.0 (s, Ar-C), 146.5 (s, Ar-C), 139.0 (s, Ar-C), 136.6 (s, Ar-C), 132.8 (s, Ar-C), 130.4 (d, 2C, 2 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 127.6 (d, Ar-CH), 124.4 (d, Ar-CH), 105.3 (d, Ar-CH), 56.1 (d, CH), 55.6 (q, Ar-OCH\(_3\)), 51.2 [s, C(CH\(_3\))\(_2\)], 25.5 [q, C(CH\(_3\))\(_2\)] ppm. HR-MS (ESI+) m/z calculated for [C\(_{18}\)H\(_{18}\)ClO\(_2\)]\(^+\)=[M+H]\(^+\): 301.0990; found 301.0988.

3-(4-bromophenyl)-6-methoxy-2,2-dimethylindan-1-one (4c) & 3-(4-bromophenyl)-4-methoxy-2,2-dimethylindan-1-one (4c'): GP-1 was carried out with ketone 1b (44.5 mg, 0.25 mmol), aldehyde 2d (92.5 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the inseparable regioisomeric mixture of indanones 4c (58.7 mg, 68%) and 4c' (14.7 mg, 17%) as a pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), \( R_f(1b) = 0.50, R_f(4c \& 4c') = 0.43 \), UV detection]. IR (MIR-ATR, 4000–600 cm\(^{-1}\)): \( \tilde{\nu}_{\text{max}} = 2964, 2925, 1710, 1602, 1488, 1465, 1270, 1242, 1011, 796 \text{ cm}^{-1} \). 1H NMR (CDCl\(_3\), 400 MHz, peaks due to major isomer 4c): \( \delta = 7.43 \) (d, 2H, \( J = 8.3 \) Hz, Ar-H), 7.26 (d, 1H, \( J = 1.9 \) Hz, Ar-H), 7.21 (dd, 1H, \( J = 8.3 \text{ and } 1.9 \) Hz, Ar-H), 7.20 (d, 1H, \( J = 8.3 \) Hz, Ar-H), 6.91 (d, 2H, \( J = 8.3 \) Hz, Ar-H), 4.22 (s, 1H, CH), 3.87 (s, 3H, Ar-OCH\(_3\)), 1.34 [s, 3H, C(CH\(_3\))\(_2\)], 0.69 [s, 3H, C(CH\(_3\))\(_2\)] ppm. 13C NMR (CDCl\(_3\), 100 MHz, peaks due to major isomer 4c): \( \delta = 210.1 \) (s, C=O), 160.0 (s, Ar-C), 146.4 (s, Ar-C), 139.5 (s, Ar-C), 131.0 (d, 2C, 2 × Ar-CH), 130.8 (d, 2C, 2 × Ar-CH), ...
127.5 (d, Ar-CH), 124.4 (d, Ar-CH), 105.3 (d, Ar-CH), 56.2 (d, CH), 55.6 (q, Ar-OCH₃), 51.2 [s, C(CH₃)₂], 25.5 [q, C(CH₃)₂a], 22.7 [q, C(CH₃)₂b] ppm. HR-MS (ESI+) m/z calculated for [C₁₈H₁₈BrO₂]⁺=[M+H]⁺: 345.0485; found 345.0484.