

## ***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

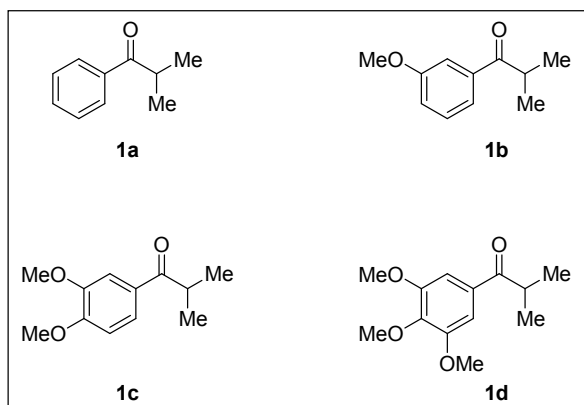
## Experimental:

**General:** IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$  ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ( $\delta_{\text{H}} = 0.00$  ppm) or  $\text{CHCl}_3$  ( $\delta_{\text{H}} = 7.25$  ppm).  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in  $\text{CDCl}_3$ ; chemical shifts ( $\delta$  ppm) are reported relative to  $\text{CHCl}_3$  [ $\delta_{\text{C}} = 77.00$  ppm (central line of triplet)]. In the  $^{13}\text{C}$  NMR, the nature of carbons (C, CH,  $\text{CH}_2$  and  $\text{CH}_3$ ) 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  $\text{CH}_2$ ) and q = quartet (for  $\text{CH}_3$ ). In the  $^1\text{H}$ -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  $^1\text{H}$ ,  $^{13}\text{C}$  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 °C was used. Dichloroethane (DCE) was dried over  $\text{CaH}_2$  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).

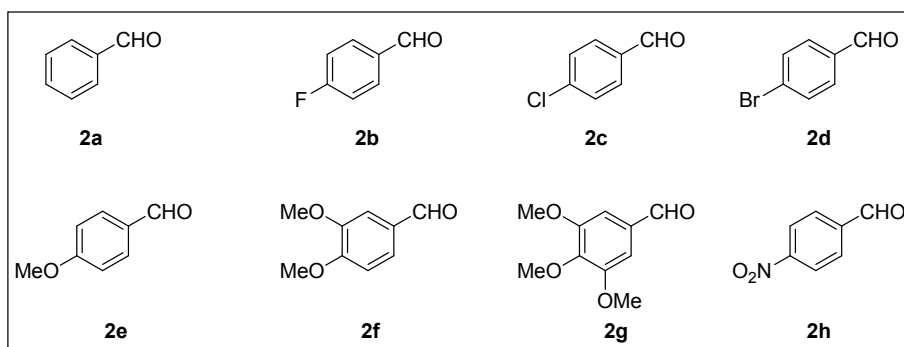
**GP-1 (General procedure for preparation of 2,2-dimethyl-3-phenylindan-1-ones 3):** In an oven dried Schlenk tube, were added ketone **1** (37.0–59.6 mg, 0.25 mmol), benzaldehyde **2** (53.0–92.5 mg, 0.50 mmol) and dichloroethane (1.5 mL) followed by triflic acid (0.11 mL, 1.25 mmol) at room temperature under nitrogen atmosphere. The reaction mixture stirred at room temperature and was then heated in an oil bath at 50 °C for 24 h (80 °C for 48 h in case of phenylisopropyl ketone) and monitored by TLC. Then, the mixture was quenched by the addition of aqueous  $\text{NaHCO}_3$  solution and then extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with saturated NaCl solution, dried ( $\text{Na}_2\text{SO}_4$ ), 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 °C for 24 h and monitored by TLC. Then, the mixture was quenched by the addition of aqueous  $\text{NaHCO}_3$  solution and then extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with saturated NaCl solution, dried ( $\text{Na}_2\text{SO}_4$ ), 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.<sup>1</sup>



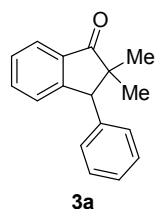
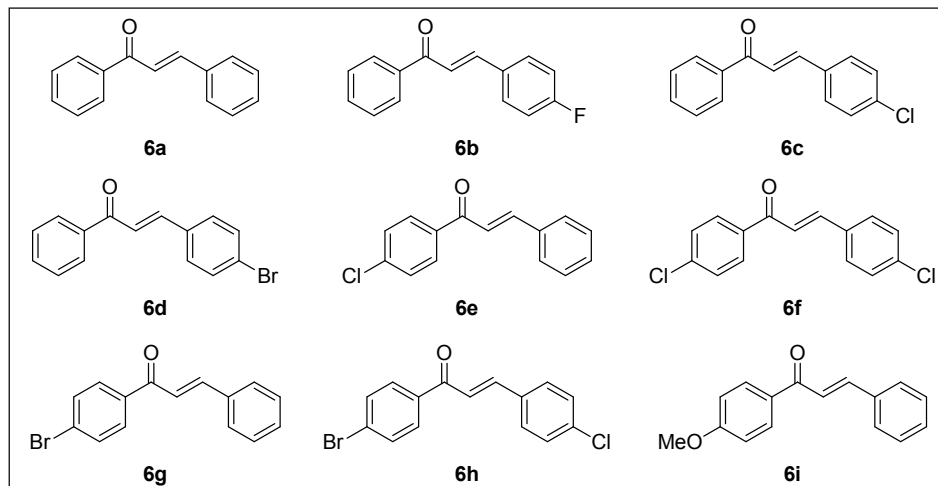
The following benzaldehydes **2a–2h**, which are used as starting materials, are commercially available.



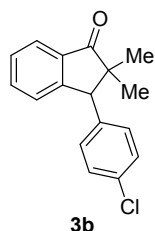
The following isopropyl ketones **6a–6i**, which have been prepared are reported in literature.<sup>2</sup>

<sup>1</sup> (a) K. Ren, B. Hu, M. Zhao, Y. Tu, X. Xie and Z. Zhang, *J. Org. Chem.*, 2014, **79**, 2170; (b) S. Ogawa and Y. Obora, *Chem. Commun.*, 2014, **50**, 2491; (c) Y. Li, D. Xue, W. Lu, C. Wang, Z.-T. Liu and J. Xiao, *Org. Lett.*, 2014, **16**, 66; (d) G. Chen, Z. Wang, J. Wu and K. Ding, *Org. Lett.*, 2008, **10**, 4573; (e) E. Brachet, A. Hamze, J.-F. Peyrat, J.-D. Brion and M. Alami, *Org. Lett.*, 2010, **12**, 4042.

<sup>2</sup> (a) Z.-W. Guo, X. Huang, J.-M. Mao, W.-D. Zhu and J.-W. Xie, *RSC Adv.*, 2013, **3**, 25103; (b) M. Gohain, J. H. van Tonder and B. C. B. Bezuidenhoudt, *Tetrahedron Lett.*, 2013, **54**, 3773; (c) D. G. Batt, R. Goodman, D. G. Jones, J. S. Kerr, L. R. Mantegna, C. McAllister, R. C. Newton, S. Nurnberg, P. K. Welch and M. B. Covington, *J. Med. Chem.*, 1993, **36**, 1434; (d) L.-M. Zhao, S.-Q. Zhang, F. Dou and R. Sun, *Org. Lett.*, 2013, **15**, 5154; (e) C.-Y. Li, Q.-S. Li, L. Yan, X.-G. Sun, R. Wei, H.-B. Gong and H.-L. Zhu, *Bioorg. Med. Chem.* 2012, **20**, 3746; (f) Y. Zhang, L. Pan, X. Xu and Q. Liu, *RSC Adv.*, 2012, **2**, 5138; (g) G. Zhang, H. Ni, W. Chen, J. Shao, H. Liu, B. Chen and Y. Yu, *Org. Lett.*, 2013, **15**, 5967; (h) S. Okusu, Y. Sugita, E. Tokunaga and N. Shibata, *Beilstein J. Org. Chem.* 2013, **9**, 2189; (i) Z. Fang, Y. Ning, P. Mi, P. Liao and X. Bi, *Org. Lett.*, 2014, **16**, 1522.

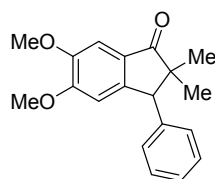


**2,2-dimethyl-3-phenylindan-1-one (3a):** GP-1 was carried out with ketone **1a** (37.0 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 80 °C for 48 h. Purification of the crude material by silica gel column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



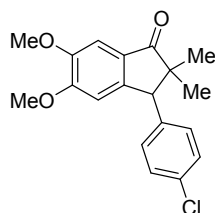
**3-(4-chlorophenyl)-2,2-dimethylindan-1-one (3b):** GP-1 was carried out with ketone **1a** (37.0 mg, 0.25 mmol), aldehyde **2c** (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol),

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),  $R_f(\mathbf{1a})=0.49$ ,  $R_f(\mathbf{3b})=0.28$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2943$ , 1714, 1604, 1491, 1443, 1375, 1090, 1038, 1014, 919, 832  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 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,  $\text{C}(\text{CH}_3)_{2a}$ ], 0.88 [s, 3H,  $\text{C}(\text{CH}_3)_{2b}$ ] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 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  $\times$  Ar-CH), 128.6 (d, 2C, 2  $\times$  Ar-CH), 127.7 (d, Ar-CH), 123.9 (d, Ar-CH), 123.6 (d, Ar-CH), 66.3 (d, CH), 43.7 [s,  $\text{C}(\text{CH}_3)_2$ ], 28.5 [q,  $\text{C}(\text{CH}_3)_{2a}$ ], 28.3 [q,  $\text{C}(\text{CH}_3)_{2b}$ ] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{17}\text{H}_{16}\text{ClO}]^+=[\text{M}+\text{H}]^+$ : 271.0884; found 271.0882.



**3c**

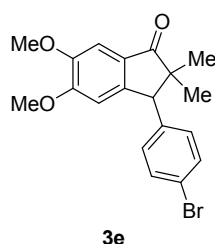
**5,6-dimethoxy-2,2-dimethyl-3-phenylindan-1-one (3c):** GP-1 was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by 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),  $R_f(\mathbf{1c})=0.45$ ,  $R_f(\mathbf{3c})=0.40$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2964$ , 2928, 1697, 1591, 1498, 1465, 1453, 1303, 1264, 1220, 1109, 1018, 911, 866, 728, 702  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 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<sub>3</sub>), 3.84 (s, 3H, Ar-OCH<sub>3</sub>), 1.32 [s, 3H,  $\text{C}(\text{CH}_3)_{2a}$ ], 0.66 [s, 3H,  $\text{C}(\text{CH}_3)_{2b}$ ] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta=209.4$  (s, C=O), 155.7 (s, Ar-C), 149.9 (s, Ar-C), 149.4 (s, Ar-C), 140.5 (s, Ar-C), 129.2 (d, 2C, 2  $\times$  Ar-CH), 128.3 (d, 2C, 2  $\times$  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<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 50.7 [s,  $\text{C}(\text{CH}_3)_2$ ], 25.8 [q,  $\text{C}(\text{CH}_3)_{2a}$ ], 22.8 [q,  $\text{C}(\text{CH}_3)_{2b}$ ] ppm.



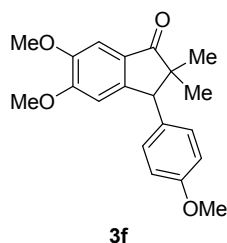
**3d**

**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

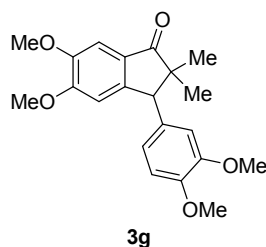
mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3d** (53.7 mg, 65%) as a palebrown solid, recrystallized the solid with dichloromethane/hexane, m. p. 110–112 °C. [TLC control (petroleum ether/ethyl acetate 80:20),  $R_f(\mathbf{1c})=0.45$ ,  $R_f(\mathbf{3d})=0.41$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2964$ , 2928, 1697, 1590, 1500, 1491, 1464, 1301, 1264, 1219, 1112, 1015, 913, 866, 845, 770, 728  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 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<sub>3</sub>), 3.84 (s, 3H, Ar-OCH<sub>3</sub>), 1.31 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.66 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 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<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 50.6 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.9 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.8 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{19}\text{H}_{20}\text{ClO}_3]^+=[\text{M}+\text{H}]^+$ : 331.1095; found 331.1095.



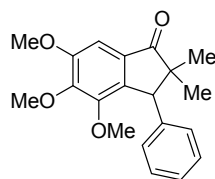
**3-(4-bromophenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3e):** GP-1 was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2d** (92.5 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (1.5 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material 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),  $R_f(\mathbf{1c})=0.45$ ,  $R_f(\mathbf{3e})=0.42$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2964$ , 2926, 2867, 1697, 1590, 1500, 1300, 1219, 1112, 1010, 729  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 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<sub>3</sub>), 3.84 (s, 3H, Ar-OCH<sub>3</sub>), 1.31 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.66 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta=208.8$  (s, C=O), 155.9 (s, Ar-C), 150.1 (s, Ar-C), 148.8 (s, Ar-C), 139.6 (s, Ar-C), 131.5 (d, 2C, Ar-CH), 130.8 (d, 2C, Ar-CH), 128.2 (s, Ar-C), 120.9 (s, Ar-C), 107.5 (d, Ar-CH), 104.5 (d, Ar-CH), 56.8 (d, CH), 56.3 (q, Ar-OCH<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 50.6 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.9 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.8 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{19}\text{H}_{20}\text{BrO}_3]^+=[\text{M}+\text{H}]^+$ : 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 palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 80:20),  $R_f(\mathbf{1c})=0.45$ ,  $R_f(\mathbf{3f})=0.34$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2963$ , 2930, 2836, 1695, 1591, 1499, 1464, 1301, 1264, 1218, 1176, 1106, 1018, 911, 726  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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-OCH<sub>3</sub>), 3.83 (s, 3H, Ar-OCH<sub>3</sub>), 3.77 (s, 3H, Ar-OCH<sub>3</sub>), 1.28 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.65 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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<sub>3</sub>), 56.1 (q, Ar-OCH<sub>3</sub>), 55.1 (q, Ar-OCH<sub>3</sub>), 50.7 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.6 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.8 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{23}\text{O}_4]^+=[\text{M}+\text{H}]^+$ : 327.1591; found 327.1591.

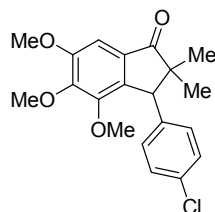


**3-(3,4-dimethoxyphenyl)-5,6-dimethoxy-2,2-dimethylindan-1-one (3g):** GP-1 was carried out with ketone **1c** (52.0 mg, 0.25 mmol), aldehyde **2f** (83.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude 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),  $R_f(\mathbf{1c})=0.53$ ,  $R_f(\mathbf{3g})=0.20$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2962$ , 2931, 2867, 2836, 1695, 1590, 1513, 1499, 1463, 1416, 1305, 1265, 1108, 1018, 866, 730, 699  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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<sub>3</sub>), 3.81 (s, 3H, Ar-OCH<sub>3</sub>), 3.80 (s, 3H, Ar-OCH<sub>3</sub>), 3.73 (s, 3H, Ar-OCH<sub>3</sub>), 1.26 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.64 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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<sub>3</sub>), 55.9 (q, Ar-OCH<sub>3</sub>), 55.7 (q, Ar-OCH<sub>3</sub>), 55.6 (q, Ar-OCH<sub>3</sub>), 50.6 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.6 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.6 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{21}\text{H}_{25}\text{O}_5]^+=[\text{M}+\text{H}]^+$ : 357.1697; found 357.1696.



**3i**

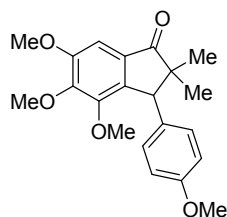
**4,5,6-trimethoxy-2,2-dimethyl-3-phenylindan-1-one (3i):** GP-1 was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2a** (53.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 85:15) furnished the indanone **3i** (70.2 mg, 86%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10),  $R_f(\mathbf{1d})=0.47$ ,  $R_f(\mathbf{3i})=0.38$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2966$ , 2935, 1703, 1602, 1469, 1342, 1313, 1123, 1087, 906, 726  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta=7.50\text{--}7.20$  (m, 6H, Ar-H), 4.41 (s, 1H, CH), 4.07 (s, 3H, Ar-OCH<sub>3</sub>), 4.05 (s, 3H, Ar-OCH<sub>3</sub>), 3.52 (s, 3H, Ar-OCH<sub>3</sub>), 1.45 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.87 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta=210.1$  (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-OCH<sub>3</sub>), 60.0 (q, Ar-OCH<sub>3</sub>), 56.2 (q, Ar-OCH<sub>3</sub>), 55.1 (d, CH), 50.7 [s, C(CH<sub>3</sub>)<sub>2</sub>], 28.3 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 21.6 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{23}\text{O}_4]^+=[\text{M}+\text{H}]^+$ : 327.1591; found 327.1590.



**3j**

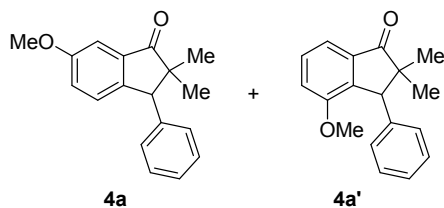
**3-(4-chlorophenyl)-4,5,6-trimethoxy-2,2-dimethylindan-1-one (3j):** GP-1 was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2c** (70.3 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the indanone **3j** (57.7 mg, 64%) as a palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10),  $R_f(\mathbf{1d})=0.47$ ,  $R_f(\mathbf{3j})=0.41$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2967$ , 2935, 1705, 1600, 1469, 1417, 1343, 1311, 1121, 1013, 912, 848, 770, 728  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta=7.50\text{--}6.10$  (m, 5H, Ar-H), 4.22 (s, 1H, CH), 3.91 (s, 3H, Ar-OCH<sub>3</sub>), 3.89 (s, 3H, Ar-OCH<sub>3</sub>), 3.43 (s, 3H, Ar-OCH<sub>3</sub>), 1.28 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.70 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta=209.6$  (s, C=O), 155.0 (s, Ar-C), 150.4 (s, Ar-C), 148.7 (s, Ar-C), 140.6 (s, Ar-C), 140.2 (s, Ar-C), 132.3 (s, Ar-C), 130.5 (s, Ar-C), 128.3 (d, 4C, Ar-CH), 100.9 (d, Ar-CH), 60.9 (q, Ar-OCH<sub>3</sub>), 60.1 (q, Ar-OCH<sub>3</sub>), 56.2 (q, Ar-OCH<sub>3</sub>), 54.4 (d, CH), 50.5 [s, C(CH<sub>3</sub>)<sub>2</sub>], 28.1 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 21.7 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{20}\text{H}_{22}\text{ClO}_4]^+=[\text{M}+\text{H}]^+$ : 361.1201; found 361.1196.



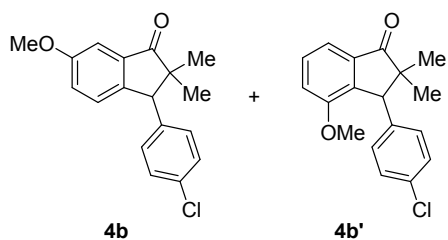


**3k**

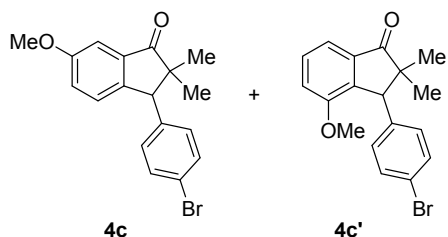
**4,5,6-trimethoxy-3-(4-methoxyphenyl)-2,2-dimethylindan-1-one (3k):** GP-1 was carried out with ketone **1d** (59.5 mg, 0.25 mmol), aldehyde **2e** (68.0 mg, 0.50 mmol), triflic acid (0.11 mL, 1.25 mmol), dichloroethane (3 mL) for the formation of indanone at 50 °C for 24 h. Purification of the crude 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 palebrown viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10),  $R_f(\mathbf{1d})=0.47$ ,  $R_f(\mathbf{3k})=0.30$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2964$ , 2933, 2837, 1704, 1600, 1511, 1467, 1417, 1342, 1310, 1244, 1121, 1033, 731  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta=7.20\text{--}6.50$  (m, 5H, Ar-H), 4.20 (s, 1H, CH), 3.91 (s, 3H, Ar-OCH<sub>3</sub>), 3.89 (s, 3H, Ar-OCH<sub>3</sub>), 3.74 (s, 3H, Ar-OCH<sub>3</sub>), 3.39 (s, 3H, Ar-OCH<sub>3</sub>), 1.27 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.71 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta=210.2$  (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-OCH<sub>3</sub>), 60.1 (q, Ar-OCH<sub>3</sub>), 56.2 (q, Ar-OCH<sub>3</sub>), 55.1 (q, Ar-OCH<sub>3</sub>), 54.4 (d, CH), 50.7 [s, C(CH<sub>3</sub>)<sub>2</sub>], 28.2 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 21.7 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{21}\text{H}_{25}\text{O}_5]^+=[\text{M}+\text{H}]^+$ : 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 regioisomeric 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),  $R_f(\mathbf{1b})=0.50$ ,  $R_f(\mathbf{4a}$  &  $\mathbf{4a}')=0.40$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2965$ , 2927, 1711, 1602, 1488, 1465, 1291, 1270, 1241, 1027, 757, 702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, peaks due to major isomer **4a**):  $\delta=7.35\text{--}7.10$  (m, 6H, Ar-H), 7.02 (d, 2H,  $J=7.3$  Hz, Ar-H), 4.26 (s, 1H, CH), 3.88 (s, 3H, Ar-OCH<sub>3</sub>), 1.35 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.69 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, peaks due to major isomer **4a**):  $\delta=210.7$  (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  $\times$  Ar-CH), 128.3 (d, 2C, 2  $\times$  Ar-CH), 127.8 (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-OCH<sub>3</sub>), 51.4 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.5 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.8 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{18}\text{H}_{19}\text{O}_2]^+=[\text{M}+\text{H}]^+$ : 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 paleyellow solid, recrystallized the solid with dichloromethane/hexane, m. p. 78–81 °C. [TLC control (petroleum ether/ethyl acetate 90:10),  $R_f(\mathbf{1b})=0.50$ ,  $R_f(\mathbf{4b} \ \& \ \mathbf{4b}')=0.42$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2963, 2926, 1707, 1599, 1488, 1465, 1270, 1241, 1089, 1013, 796 \text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, peaks due to major isomer **4b**):  $\delta=7.32\text{--}7.17$  (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<sub>3</sub>), 1.34 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.69 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 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  $\times$  Ar-CH), 128.5 (d, 2C, 2  $\times$  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<sub>3</sub>), 51.2 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.5 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.7 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+)  $m/z$  calculated for  $[\text{C}_{18}\text{H}_{18}\text{ClO}_2]^+=[\text{M}+\text{H}]^+$ : 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 paleyellow viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10),  $R_f(\mathbf{1b})=0.50$ ,  $R_f(\mathbf{4c} \ \& \ \mathbf{4c}')=0.43$ , UV detection]. IR (MIR-ATR, 4000–600  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}=2964, 2925, 1710, 1602, 1488, 1465, 1270, 1242, 1011, 796 \text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 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,  $J=8.3$  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<sub>3</sub>), 1.34 [s, 3H, C(CH<sub>3</sub>)<sub>2a</sub>], 0.69 [s, 3H, C(CH<sub>3</sub>)<sub>2b</sub>] ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 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), 136.6 (s, Ar-C), 131.4 (d, 2C, 2  $\times$  Ar-CH), 131.0 (s, Ar-C), 130.8 (d, 2C, 2  $\times$  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-OCH<sub>3</sub>), 51.2 [s, C(CH<sub>3</sub>)<sub>2</sub>], 25.5 [q, C(CH<sub>3</sub>)<sub>2a</sub>], 22.7 [q, C(CH<sub>3</sub>)<sub>2b</sub>] ppm. HR-MS (ESI+) m/z calculated for [C<sub>18</sub>H<sub>18</sub>BrO<sub>2</sub>]<sup>+</sup>=[M+H]<sup>+</sup>: 345.0485; found 345.0484.