Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information:

Lewis acid promoted C–C and Copper-catalyzed C–O bonds formation: Synthesis of neoflavans

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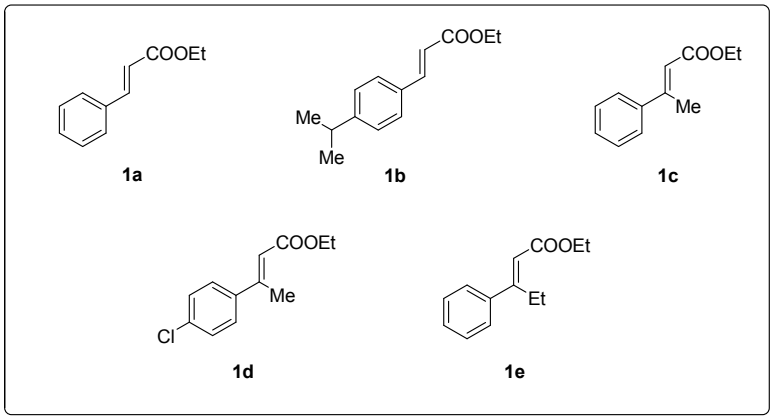
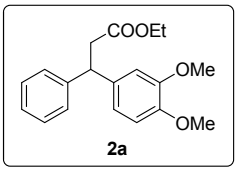
General: IR spectra were recorded on a Bruker Tensor 37 (FT-IR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ in ppm) and coupling constants (J in Hz) are reported in standard fashion with reference to either internal 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 in 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, septd = septet of doublets. 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 using multimode source. All small scale dry reactions were carried out using standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a mixture of petroleum ether and ethyl acetate as eluents. Reactions were generally run under an argon or nitrogen atmosphere. All Solvents were distilled prior use; petroleum ether with a boiling range of 60 to 80 ˚C, dichloromethane (DCM), ethyl acetate, methanol, tetrahydrofuran (THF), diethyl ether, DMF, purchased from locally available commercial sources were used. All aromatic aldehydes, bromine, Calcium hydride, $FeCl_3$, 4Å Molecular sieves, sodium metal, silica gel (60–120 mesh) purchased from locally available commercial sources were used. Copper iodide, 2, 2'-bipyridine LAH, were purchased from sigma-Aldrich used without further purification. THF and diethyl ether and dried over sodium, DCM, DCE and DMF dried over calcium hydride (CaH_2). Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

The following cinnamates **1b**,[1] **1c**,[2] **1d**[3] and **1e**[4] reported in the literature whereas **1a** commercially available.



General Procedure-1 for arylations of Ethyl Cinnamates (2a-2f): To an oven dried RBF under nitrogen atmosphere, were added ester **1a-1e** (5.00 mmol), varatrole or trimethoxybenzene (7.50 mmol) and DCM (8 mL), followed by the addition of $FeCl_3$ (15.00 mmol). The resultant reaction mixture was stirred at rt for 12 h. The reaction mixture was quenched by the addition of aqueous $NaHCO_3$ and extracted with DCM (3 × 100 mL). The combined organic layers were washed with saturated NaCl solution, then dried over anhydrous Na_2SO_4 then it was concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the arylated ester **2a-2f** (47–87%).



2a

ethyl 3-(3,4-dimethoxyphenyl)-3-phenylpropanoate (**2a**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1a** (881 mg, 5.00 mmol), varatrole (1.03 g, 7.50 mmol) and $FeCl_3$ (2.43 g, 15.00 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 92:08 to 85:15) furnished the arylated ester **2a** (1.05 g, 67%) as colorless viscous liquid. [TLC control R_f(**1a**)=0.60, R_f(**varatrole**)=0.40, R_f(**2a**)=0.20 (petroleum ether/ethyl acetate 90:10, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2924, 2851, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.33–7.15 (m, 5H, Ar-H), 6.79 (s, 2H, Ar-H), 6.74 (s, 1H, Ar-H), 4.50 (t, 1H, *J*=7.8 Hz, ArC*H*CH_2COOEt), 4.04 (q, 2H, *J*=7.3 Hz, OC*H*$_2CH_3$), 3.84 (s, 3H, Ar-OCH_3), 3.82 (s, 3H, Ar-OCH_3), 3.02 (d, 2H, *J*=7.8 Hz, C*H*$_2$COOEt), 1.13 (t, 3H, *J*=7.3 Hz, OCH_2C*H*$_3$)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.8 (s, O=C–O), 148.8 (s, Ar-C), 147.5 (s, Ar-C), 143.6 (s, Ar-C), 136.0 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 127.5 (d, 2C, Ar-CH), 126.4 (d, Ar-CH), 119.3 (d, Ar-CH), 111.2 (d, Ar-CH), 111.0 (d, Ar-CH), 60.4 (t, O*C*H$_2CH_3$), 55.8 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 46.6 (d, Ar*C*HCH$_2$COOEt), 41.0 (t, *C*H$_2$COOEt), 14.0 (q, OCH_2*C*H$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{21}O_3]^+$=$[(M+H)–H_2O]^+$: 297.1485; found: 297.1479.

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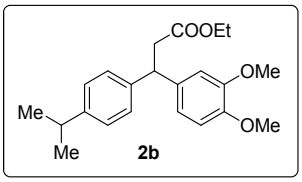
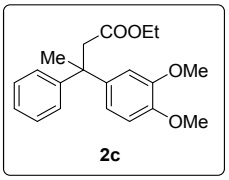
[1]Gomes, P.; Gosmini, C.; Nedelec, J.-Y.; Perichon, J.; *Tetrahedron Lett*. **2002**, *43*, 5901–5903.
[2]Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. *Org. Lett*. **2003**, *5*, 2417–2420.
[3]Duan, Z-C.; Hu, X-P Zhang, C.; Zheng, Z. *J. Org. Chem*. **2010**, *75*, 8319–8321.
[4]Kraus, A.; Ghorai, P.; Birnkammer, T.; Schnell, D.; Elz, S.; Seifert, R.; Dove, S.; Bernhardt, G.; Buschauer , A. *Chem. Med. Chem*. **2009**, *4*, 232–240.

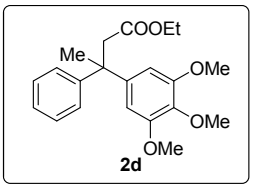


ethyl 3-(3,4-dimethoxyphenyl)-3-(4-isopropylphenyl)propanoate (**2b**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1b** (1.09 g, 5.00 mmol), varatrole (1.03 g, 7.50 mmol) and $FeCl_3$ (2.42 g, 15 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the arylated ester **2b** (1.55 g, 87%) as colorless viscous liquid. [TLC control R_f(**1b**)=0.85, R_f(varatrole)=0.75, R_f(**2b**)=0.60, (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2976, 2935, 2836, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.14 (d, 2H, *J*=8.8 Hz, Ar-H), 7.13 (d, 2H, *J*=8.8 Hz, Ar-H), 6.79 (d, 1H, *J*=8.3 Hz, Ar-H), 6.78 (d, 1H, *J*=8.3 Hz, Ar-H), 6.75 (br. s, 1H, Ar-H), 4.45 (t, 1H, *J*=8.3 Hz, ArC*H*CH_2COOEt), 4.02 (q, 2H, *J*=7.3 Hz, OC*H*$_2CH_3$), 3.83 (s, 3H, Ar-OCH_3), 3.82 (s, 3H, Ar-OCH_3), 2.99 (d, 2H, *J*=8.3 Hz, ArCHC*H*$_2$COOEt), 2.81 [sept, 1H, *J*=6.8 Hz, C*H*$(CH_3)_2$], 1.20 [d, 6H, *J*=6.8 Hz, CH(C*H*$_3)_2$], 1.11 (t, 3H, *J*=7.3 Hz, OCH_2C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.9 (s, O=C–O), 148.7 (s, Ar-C), 147.5 (s, Ar-C), 146.9 (s, Ar-C), 141.0 (s, Ar-C), 136.2 (s, Ar-C), 127.2 (d, 2C, Ar-CH), 126.5 (d, 2C, Ar-CH), 119.4 (d, Ar-CH), 111.2 (d, Ar-CH), 111.0 (d, Ar-CH), 60.3 (t, O*C*H_2CH_3), 55.8 (q, 2C, 2 × Ar-OCH_3), 46.3 [d, Ar*C*H(Ar)CH_2COOEt], 41.1 [t, ArCH(Ar)*C*H_2COOEt], 33.6 [d, *C*H$(CH_3)_2$], 22.9 [q, 2C, CH(*C*$H_3)_2$], 14.0 (q, OCH_2*C*H_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{29}O_4]^+$=$[M+H]^+$: 357.2060; found: 357.2046.

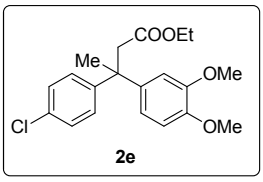


ethyl 3-(3,4-dimethoxyphenyl)-3-phenylbutanoate (**2c**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1c** (951 mg, 5.00 mmol), varatrole (1.03 g, 7.5 mmol) and $FeCl_3$ (2.43 mg, 15.00 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 92:08 to 85:15) furnished the arylated ester **2c** (1.2 g, 71%). [TLC control R_f(**1c**)=0.90, R_f(varatrole)=0.85, R_f(**2c**)=0.75, (petroleum ether/ethyl acetate 80:20, UV detection)].
Compound 2C[5] reported in literature

[5]Ramulu, B. V.; Reddy, A. G. K.; Satyanarayana, G. *Synlett* **2013**, *24*, 0868–0872.

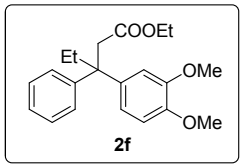


ethyl 3-phenyl-3-(3,4,5-trimethoxyphenyl)butanoate (**2d**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1c** (915 mg, 5.00 mmol) trimethoxybenzene (1.26 mg, 7.50 mmol) and $FeCl_3$ (2.43 mg, 15.00 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 85:15 to 80:20) furnished the arylated ester **2d** (842 mg, 47%) as colorless viscous liquid. [TLC control R_f(**1c**)=0.90, R_f(trimethoxybenzene)=0.60, R_f(**2d**)=0.40, (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2975, 2933, 1727, 1570, 1463, 1366, 1279, 1208, 1028, 677, 603, 563 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, *J*=8.3 and 5.3 Hz, Ar-H), 7.20 (d, 2H, *J*=7.3 Hz, Ar-H), 7.19 (t, 1H, *J*=7.3 Hz, Ar-H), 6.39 (s, 2H, Ar-H), 3.88 (q, 2H, *J*=7.3 Hz, OCH_2CH_3), 3.82 (s, 3H, Ar-OCH_3), 3.75 (s, 6H, 2 × Ar-OCH_3), 3.08 (s, 2H, CH_2COOEt), 1.86 [s, 3H, $ArCCH_3$], 0.98 (t, 3H, *J*=7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.3 (s, O=C–O), 152.5 (s, 2C, Ar-C), 148.1 (s, Ar-C), 143.9 (s, Ar-C), 136.3 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 126.9 (d, 2C, Ar-CH), 126.1 (d, Ar-CH), 104.9 (d, 2C, Ar-CH), 60.8 (q, Ar-OCH_3), 60.0 (t, OCH_2CH_3), 56.1 (q, 2C, Ar-OCH_3), 46.7 [s, $ArC(CH_3)CH_2COOEt$], 45.7 [s, $ArC(CH_3)CH_2COOEt$], 28.4 [q, $ArC(CH_3)CH_2COOEt$], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{30}NO_5]^+$=$[M+NH_4]^+$: 376.2118; found: 376.2114.



ethyl 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)butanoate (**2e**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1d** (1.12 g, 5.00 mmol), varatrole (1.03 mg, 7.50 mmol) and $FeCl_3$ (2.42 g, 15.00 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the arylated ester **2e** (1.12 mg, 62%) as colorless viscous liquid. [TLC control R_f(**1d**)=0.80, R_f(varatrole)=0.75, R_f(**2e**)=0.55, (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2976, 2935, 2836, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.22 (d, 2H, *J*=8.8 Hz, Ar-H), 7.12 (d, 2H, *J*=8.8, Ar-H), 6.77 (d, 1H, *J*=8.8 Hz, Ar-H), 6.75 (dd, 1H, *J*=8.8 and 2.0 Hz, Ar-H), 6.61 (d, 1H, *J*=2.0 Hz, Ar-H), 3.89 (q, 2H, *J*=7.3 Hz, OCH_2CH_3), 3.84 (s, 3H, Ar-OCH_3), 3.75 (s, 3H, Ar-OCH_3), 3.05 (s, 2H, CH_2COOEt), 1.82 [s, 3H, $ArC(CH_3)$], 1.0 (t, 3H, *J*=7.3 Hz,

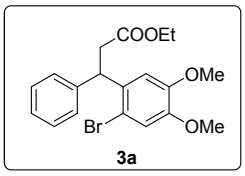
OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.0 (s, O=C–O), 148.4 (s, Ar-C), 147.4 (s, Ar-C), 146.9 (s, Ar-C), 140.4 (s, Ar-C), 129.2 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 128.0 (d, 2C, Ar-CH), 118.9 (d, Ar-CH), 110.9 (d, Ar-CH), 110.5 (d, Ar-CH), 60.1 (t, OCH_2CH_3), 55.8 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 46.6 (t, CH_2COOEt), 44.9 [s, Ar$C(CH_3)CH_2COOEt$], 28.4 [q, Ar$C(CH_3)CH_2COOEt$], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{23}ClKO_4]^+$=$[M+K]^+$: 401.0916; found: 401.0917.



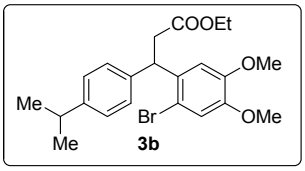
2f

ethyl 3-(3,4-dimethoxyphenyl)-3-phenylpentanoate (**2f**): General procedure-1 was carried out in an oven dried RBF under nitrogen atmosphere, were added ester **1e** (1.02 g, 5.00 mmol), varatrole (1.01 g, 7.50 mmol) and $FeCl_3$ (2.43 mg, 15.00 mmol), followed by addition of dry DCM (8 mL). Purification of the residue by silica gel column chromatography (petroleum ether/ethyl acetate 90:10 to 85:15) furnished the arylated ester **2f** (1.36 g, 80%) as colorless viscous liquid. [TLC control R_f(**1e**)=0.90, R_f(varatrole)=0.75, R_f(**2f**)=0.60 (petroleum ether/ethyl acetate 80:20, UV detection)]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2924, 2851, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.23 (dd, 2H, J=7.8 and 6.8 Hz, Ar-H), 7.18 –7.10 (m, 3H, Ar-H), 6.75 (dd, 2H, J=8.3 and 2.0 Hz, Ar-H), 6.58 (d, 1H, J=2.0 Hz, Ar-H), 3.83 (s, 3H, Ar-OCH_3), 3.80 (q, 2H, J=7.3 Hz, OCH_2CH_3), 3.71 (s, 3H, Ar-OCH_3), 3.05 (s, 2H, CH_2COOEt), 2.33 [q, 2H, J=7.3 Hz, Ar$C(CH_2CH_3)$], 0.91 (t, 3H, J=7.3 Hz, OCH_2CH_3), 0.72 [t, 3H, J=7.3, Ar$C(CH_2CH_3)$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.4 (s, O=C–O), 148.2 (s, Ar-C), 147.3 (s, Ar-C), 147.1 (s, Ar-C), 139.8 (s, Ar-C), 127.7 (d, 2C, Ar-CH), 127.6 (d, 2C, Ar-CH), 125.9 (d, Ar-CH), 119.8 (d, Ar-CH), 111.7 (d, Ar-CH), 110.1 (d, Ar-CH), 59.9 (t, OCH_2CH_3), 55.8 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 48.8 [s, Ar$C(CH_2CH_3)CH_2COOEt$], 42.4 (t, CH_2COOEt), 30.6 [t, Ar$C(CH_2CH_3)CH_2COOEt$], 13.8 (q, OCH_2CH_3), 8.7 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{26}NaO_4]^+$=$[M+Na]^+$: 365.1723; found: 365.1723.

General Procedure-2 for bromination of aryl Ethyl Cinnamates (3a-3f): To an oven dried RBF under nitrogen atmosphere, were added ester **2a-2f** (3.00 mmol) in 20 mL of dry DCM, was added Bromine (3.30 mmol) in 20 mL of dry DCM drop wise at 0 ˚C and the resultant reaction mixture was stirred for at 0 ˚C 4 h. The reaction mixture was quenched by the addition of aqueous $Na_2S_2O_3$ and organic layers were washed with saturated $NaHCO_3$ solution and followed by saturated NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the bromoester **3a-3f** (90-97%)

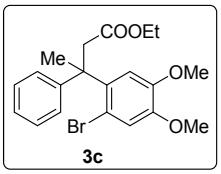


ethyl 3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylpropanoate (**3a**): General procedure-2 was carried out with ester **2a** (943 mg, 3.00 mmol) in dry DCM 20 mL, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the title compound **3a** (1.14 g, 97%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**2a**)=0.45, R_f(**3a**)=0.45, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2977, 2934, 1731, 1602, 1503, 1440, 1257, 1161, 1029, 857, 797, 702, 594 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.40–7.12 (m, 5H, Ar-H), 6.99 (s, 1H, Ar-H), 6.70 (s, 1H, Ar-H), 4.96 (t, 1H, J=7.8 Hz, ArC*H*CH_2COOEt), 4.02 (q, 2H, J=7.3 Hz, OC*H*$_2$$CH_3$), 3.80 (s, 3H, Ar-$OCH_3$), 3.77 (s, 3H, Ar-$OCH_3$), 2.99 (d, 2H, J=7.8 Hz, ArCHC*H*$_2$), 1.10 (t, 3H, J=7.3 Hz, OCH_2C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.3 (s, O=C–O), 148.4 (s, Ar-C), 148.1 (s, Ar-C), 142.2 (s, Ar-C), 134.2 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 127.6 (d, 2C, Ar-CH), 126.6 (d, Ar-CH), 115.7 (d, Ar-CH), 114.6 (s, Ar-C), 111.2 (d, Ar-CH), 60.5 (t, O*C*H_2CH_3), 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 45.3 (t, *C*H_2COOEt), 40.4 (d, Ar*C*HCH$_2$COOEt), 14.0 (q, OCH_2*C*H_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{21}BrNaO_4]^+$=$[M+Na]^+$: 415.0515; found: 415.0501.



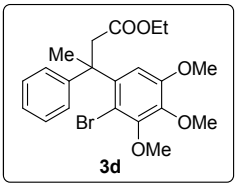
ethyl 3-(2-bromo-4,5-dimethoxyphenyl)-3-(4-isopropylphenyl)propanoate (**3b**): General procedure-2 was carried out with ester **2b** (1.06 g, 3.00 mmol) in dry 20 mL of DCM, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the title compound **3b** (1.21 g, 93%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 85:15), R_f(**2b**)=0.65, R_f(**3b**)=0.50, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2976, 2935, 2836, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.14 (d, 2H, J=8.3 Hz, Ar-H), 7.13 (d, 2H, J=8.3 Hz, Ar-H), 7.00 (s, 1H, Ar-H), 6.73 (s, 1H, Ar-H), 4.95 (t, 1H, J=7.8 Hz, ArC*H*CH_2COOEt), 4.05 (q, 2H, J=7.3 Hz, OC*H*$_2$$CH_3$), 3.82 (s, 3H, $ArOCH_3$), 3.80 (s, 3H, $ArOCH_3$), 2.99 (d, 2H, J=7.8 Hz, ArCHC*H*$_2$COOEt), 2.84 [sept, 1H, J=6.8 Hz, ArC*H*$(CH_3)_2$], 1.21[d, 6H, J=6.8 Hz, ArCH(C*H*$_3$)$_2$], 1.12 (t, 3H, J=7.3 Hz, OCH_2C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.4 (s, O=C–O), 148.4 (s, Ar-C), 148.0 (s, Ar-C), 147.1 (s, Ar-C), 139.5 (s, Ar-C), 134.4 (s, Ar-C), 127.4 (d, 2C, Ar-CH), 126.5 (d, 2C, Ar-CH), 115.7

(d, Ar-CH), 114.6 (s, Ar-C), 111.2 (d, Ar-CH), 60.5 (t, O*C*H$_2$CH$_3$), 56.1 (q, ArOCH$_3$), 56.0 (q, ArOCH$_3$), 44.9 [d, Ar*C*H(Ar)CH$_2$COOEt], 40.6 [t, ArCH(Ar)*C*H$_2$COOEt], 33.6 [d, Ar*C*H(CH$_3$)$_2$], 23.9 [q, 2C, ArCH(*C*H$_3$)$_2$], 14.0 (q, OCH$_2$*C*H$_3$) ppm. HR-MS (ESI+) m/z calculated for [$C_{22}H_{27}BrKO_4$]$^+$=[M+K]$^+$: 473.0724; found: 473.0709.



3c

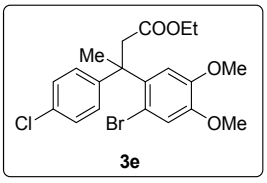
ethyl 3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylbutanoate (**3c**): General procedure-2 was carried out with ester **2c** (985 mg, 3.00 mmol) in dry 20 mL DCM, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL of DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the title compound **3c** (1.14 mg, 94%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R$_f$(**2c**)=0.75, R$_f$(**3c**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2975, 2933, 1727, 1570, 1463, 1366, 1279, 1208, 1028, 677, 603, 563 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.25 (dd, 2H, *J*=6.8 and 1.5 Hz, Ar-H), 7.17 (t, 1H, *J*=7.3 Hz, Ar-H), 7.13 (s, 1H, Ar-H), 7.09 (dd, 2H, *J*=6.8 and 1.5 Hz, Ar-H), 6.97 (s, 1H, Ar-H), 3.91 (s, 3H, Ar-OCH$_3$), 3.85 (q, 2H, *J*=7.3 Hz, OC*H*$_2$CH$_3$), 3.83 (s, 3H, ArOCH$_3$), 3.79 [d, 1H, *J*=13.2 Hz, ArC(CH$_3$)CH$_a$*H*$_b$], 3.02 [d, 1H, *J*=13.2 Hz, ArC(CH$_3$)C*H*$_a$H$_b$], 1.88 [s, 3H, ArC(CH$_3$)], 0.96 (t, 3H, *J*=7.3 Hz, OCH$_2$C*H*$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=171.4 (s, O=C–O), 148.6 (s, Ar-C), 147.9 (s, Ar-C), 147.3 (s, Ar-C), 136.4 (s, Ar-C), 128.2 (d, 2C, Ar-CH), 126.0 (d, 2C, Ar-CH), 125.7 (d, Ar-CH), 118.0 (d, Ar-CH), 114.4 (s, Ar-C), 113.2 (d, Ar-CH), 60.0 (t, O*C*H$_2$CH$_3$), 56.1 (q, Ar-OCH$_3$), 56.0 (q, Ar-OCH$_3$), 46.6 [s, Ar*C*(CH$_3$)CH$_2$COOEt], 43.5 (t, *C*H$_2$COOEt), 30.6 [q, ArC(*C*H$_3$)CH$_2$COOEt], 13.9 (q, OCH$_2$*C*H$_3$) ppm. HR-MS (ESI+) m/z calculated for [$C_{20}H_{27}BrNO_4$]$^+$=[M+NH$_4$]$^+$: 424.1118; found: 424.1103.



3d

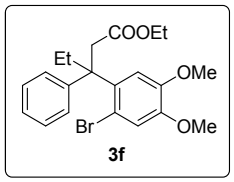
ethyl 3-(2-bromo-3,4,5-trimethoxyphenyl)-3-phenylbutanoate (**3d**): General procedure-2 was carried out with ester **2d** (1.07 g, 3.00 mmol) in 20 mL dry DCM, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL of dry DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 70:30) furnished the title compound **3d** (1.20 mg, 95%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R$_f$(**2d**)=0.40, R$_f$(**3d**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2975, 2933, 1727, 1570, 1463, 1366, 1279, 1208, 1028, 677, 603, 563 cm^{-1}. ^{1}H NMR

($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, J=7.3 and 5.9 Hz, Ar-H), 7.17 (t, 1H, J=7.3 Hz, Ar-H), 7.07 (d, 2H, J=7.3 Hz Ar-H), 6.99 (s, 1H, Ar-H), 3.91 (s, 3H, Ar-OCH_3), 3.89 (s, 3H, Ar-OCH_3), 3.87–3.81 (m, 3H, CH_aH$_b$COOCH_2CH$_3$), 3.79 (s, 3H, Ar-OCH_3), 3.02 (d, 1H, J=13.2 Hz, CH$_a$$H_b$COOEt), 1.89 [s, 3H, ArC(CH_3)], 0.94 (t, 3H, J=7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.4 (s, O=C–O), 151.5 (s, Ar-C), 151.4 (s, Ar-C), 148.5 (s, Ar-C), 141.8 (s, Ar-C), 140.0 (s, Ar-C), 128.2 (d, 2C, Ar-CH), 125.9 (d, 2C, Ar-CH), 125.7 (s, Ar-C), 111.7 (d, Ar-CH), 109.5 (d, Ar-CH), 61.0 (q, Ar-OCH_3), 60.7 (t, OCH_2CH_3), 60.0 (q, Ar-OCH_3), 56.2 (q, Ar-OCH_3), 47.5 [s, ArC(CH_3)CH_2COOEt], 43.5 [t, ArC(CH_3)CH_2COOEt], 30.8 [q, ArC(CH_3)CH_2COOEt], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{25}BrKO_5]^+$=$[M+K]^+$: 475.0517; found: 475.0507.



3e

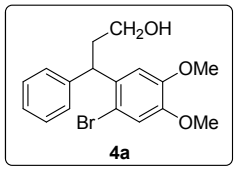
ethyl 3-(2-bromo-4,5-dimethoxyphenyl)-3-(4-chlorophenyl)butanoate (**3e**): General procedure-2 was carried out with ester **2e** (1.08 g, 3.00 mmol) in 20 mL of dry DCM, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL of dry DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20) furnished the title compound **3e** (1.19 g, 90%) as white solid, recrystallized the solid in dichloromethane/hexane m. p. 104–106 ˚C. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**2e**)=0.55, R_f(**3e**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2976, 2933, 2841, 1727, 1599, 1572, 1503, 1493, 1462, 1440, 1401, 1367, 1316, 1252, 1208, 1174, 1095, 1029, 1012, 951, 920, 854, 827, 794, 722, 704, 626 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.21 (dd, 2H, J=8.8 and 2.0 Hz, Ar-H), 7.10 (s, 1H, Ar-H), 7.00 (dd, 2H, J=8.8 and 2.0 Hz, Ar-H), 6.97 (s, 1H, Ar-H), 3.91 (s, 3H, Ar-OCH_3), 3.86 (q, 2H, J=7.3 Hz, OCH_2CH_3), 3.84 (s, 3H, ArOCH_3), 3.72 (d, 1H, J=13.2 Hz, CH_aH$_b$COOEt), 2.99 (s, 1H, J=13.2 Hz, CH$_a$$H_b$COOEt), 1.85 [s, 3H, ArC(CH_3)], 0.97 (t, 3H, J=7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.1 (s, O=C–O), 148.1 (s, Ar-C), 147.4 (s, Ar-C), 147.2 (s, Ar-C), 136.0 (s, Ar-C), 131.5 (s, Ar-C), 128.3 (d, , 2CAr-CH), 127.6 (d, 2C, Ar-CH), 118.1 (d, Ar-CH), 114.3 (s, Ar-C), 113.0 (d, Ar-CH), 60.1 (t, OCH_2CH_3), 56.1 (q, ArOCH_3), 56.0 (q, Ar-OCH_3), 46.3 [s, ArC(CH_3)CH_2COOEt], 43.7 (t, CH$_2$COOEt), 30.3 [q, ArC(CH$_3$)CH_2COOEt], 13.9 (q, OCH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{22}BrClNaO_4]^+$=$[M+Na]^+$: 463.0282; found: 463.0271.



3f

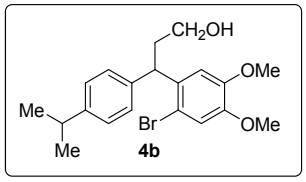
ethyl 3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylpentanoate (**3f**): General procedure-2 was carried out with ester **2f** (1.02 g, 3.00 mmol) in 20 mL of dry DCM, was added Bromine (0.17 mL, 3.30 mmol) in 20 mL of dry DCM drop wise at 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the title compound **3f** (1.16 g, 92%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**2f**)=0.60, R_f(**3f**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2960, 2924, 2851, 1730, 1590, 1516, 1491, 1463, 1410, 1367, 1336, 1255, 1216, 1175, 1147, 1095, 1067, 1023, 1012, 832, 806, 767 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, *J*=7.3 and 1.5 Hz, Ar-H), 7.16 (t, 1H, *J*=7.3 Hz, Ar-H), 7.14 (s, 1H, Ar-H), 7.04 (dd, 2H, *J*=6.8 and 1.5 Hz, Ar-H), 6.99 (s, 1H, Ar-H), 3.93 (s, 3H, Ar-OCH_3), 3.84 (s, 3H, Ar-OCH_3), 3.82 (q, 2H, *J*=7.3 Hz, O*C*$H_2$$CH_3$), 3.63 (d 1H, *J*=13.2 Hz, *C*H_2COOEt), 3.08 (d,1H, *J*=13.2 Hz, *C*H_2COOEt), 2.66 [q, 1H, *J*=7.3 Hz, ArCC$H_a$$H_b$$CH_3$], 2.19 [q, 1H, *J*=7.3 Hz, ArCC$H_a$$H_b$$CH_3$], 0.94 [t, 3H, *J*=7.3, ArC(CH_2CH_3)], 0.71 (t, 3H, *J*=7.3 Hz, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.4 (s, O=C–O), 147.7 (s, Ar-C), 147.1 (s, Ar-C), 145.9 (s, Ar-C), 136.4 (s, Ar-C), 127.7 (d, 2C, Ar-CH), 127.3 (d, 2C, Ar-CH), 125.7 (d, Ar-CH), 118.2 (d, Ar-CH), 114.7 (s, Ar-C), 113.5 (d, Ar-CH), 59.9 (t, O*C*$H_2$$CH_3$), 56.1 (q, Ar-$OCH_3$), 56.0 (q, Ar-$OCH_3$), 49.7 [s, Ar*C*($CH_2CH_3$)$CH_2$COOEt], 39.7 (t, *C*$H_2$COOEt), 30.9 [t, ArC(*C*$H_2$$CH_3$)$CH_2$COOEt], 13.9 (q, OCH_2*C*H_3), 8.9 (q, CH_2*C*H_3)ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{25}BrNaO_4]^+$=$[M+Na]^+$: 443.0828; found: 443.0819.

General Procedure-3 for reduction of Ethyl Cinnamates (4a-4f): To an oven dried RBF under nitrogen atmosphere, were added bromoster **3a-3f** (0.50 mmol) in dry ether (25 mL), was added slowly $LiAlH_4$ (1.50 mmol) in portion wise 0 ˚C and the resultant reaction mixture was stirred for at 0 ˚C 1 h. then it was quenched with ethyl acetate, separated the organic layer and aqueous, extracted the aqueous layer with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography, furnished the primary alcohol **4a-4f** (89-94%).

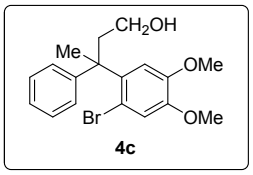


4a

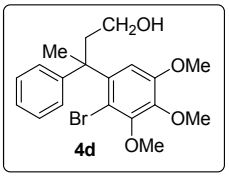
3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylpropan-1-ol (**4a**): General procedure-3 was carried out with ester **3a** (196 mg, 0.50 mmol) in 25 mL of dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25 to 70:30) furnished the title compound **4a** (158 mg, 90%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**3a**)=0.60, R_f(**4a**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3384, 2933, 2841, 1601, 1500, 1452, 1439, 1377, 1257, 1210, 1158, 1027, 700, 606 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.38–7.24 (m, 4H, Ar-H), 7.23–7.10 (m, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.73 (s, 1H, Ar-H), 4.58 (t, 1H, *J*=7.8 Hz, ArC*H*CH_2), 3.82 (s, 3H, Ar-OCH_3), 3.78 (s, 3H, Ar-OCH_3), 3.61 (t, 2H, *J*=6.8 Hz, CH_2C*H*$_2$OH), 2.40–2.14 (m, 2H, ArCHC*H*$_2CH_2$OH), 1.65 (br. s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.6 (s, Ar-C), 148.0 (s, Ar-C), 143.3 (s, Ar-C), 135.5 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 127.8 (d, 2C, Ar-CH), 126.4 (d, Ar-CH), 115.5 (d, Ar-CH), 114.7 (s, Ar-C), 111.3 (d, Ar-CH), 60.9 (t, CH_2*C*H_2OH), 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 45.1 (d, Ar*C*HCH_2CH_2OH), 38.2 (t, ArCH*C*H_2CH_2OH) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{17}{}^{81}BrKO_2]^+$=$[M+K-H_2O]^+$: 350.0523; found: 350.0532.



3-(2-bromo-4,5-dimethoxyphenyl)-3-(4-isopropylphenyl)propan-1-ol (**4b**): General procedure-3 was carried out with ester **3b** (217 mg, 0.50 mmol) in 25 mL of dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 40:60 to 30:70) furnished the title compound **4b** (175 mg, 89%) colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 60:40), R_f(**3b**)=0.80, R_f(**4b**)=0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3352, 2922, 2851, 1619, 1506, 1462, 1439, 1258, 1212, 1159, 1029, 759, 701, 670 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.19 (d, 2H, *J*=8.3 Hz, Ar-H), 7.15 (d, 2H, *J*=8.3 Hz, Ar-H), 6.99 (s, 1H, Ar-H), 6.73 (s, 1H, Ar-H), 4.55 (t,1H, *J*=7.8 Hz, ArC*H*CH_2CH_2OH), 3.82 (s, 3H, Ar-OCH_3), 3.79 (s, 3H, Ar-OCH_3), 3.61 (t, 2H, *J*=6.8 Hz, CH_2C*H*$_2$OH), 2.85 [sept, 1H, *J*=6.8 Hz, ArC*H*$(CH_3)_2$], 2.36–2.15 (m, 2H, CHC*H*$_2CH_2$OH), 1.70 (br. s, 1H, OH), 1.22 [d, 6H, *J*=6.8 Hz, ArCH(C*H*$_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.7 (s, Ar-C), 148.0 (s, Ar-C), 146.9 (s, Ar-C), 140.6 (s, Ar-C), 135.7 (s, Ar-C), 127.6 (d, 2C, Ar-CH), 126.6 (d, 2C, Ar-CH), 115.5 (d, Ar-CH), 114.7 (s, Ar-C), 111.3 (d, Ar-CH), 61.0 (t, CH_2*C*H_2OH), 56.1 (q, Ar-O*C*H_3), 56.0 (q, Ar-O*C*H_3), 44.8 [d, Ar*C*H(Ar)CH_2CH_2OH], 38.3 [t, ArCH(Ar)*C*H_2CH_2OH], 33.6 [d, Ar*C*H$(CH_3)_2$], 24.0 [q, 2C, ArCH(*C*$H_3)_2$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{25}BrNaO_3]^+$=$[M+Na]^+$: 415.0879; found: 415.0872.

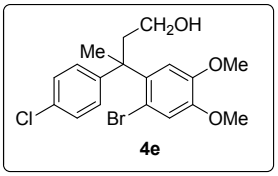


3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylbutan-1-ol (**4c**): General procedure-3 was carried out with ester **3c** (203 mg, 0.50 mmol) in 25 mL of dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 60:40 to 50:50) furnished the title compound **4c** (168 mg, 92%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**3c**)=0.80, R_f(**4c**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3373, 2935, 2840, 2599, 1570, 1503, 1462, 1408, 1376, 1364, 1317, 1283, 1251, 1210, 1165, 1133, 860, 766, 701, 611 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, J=7.3 and 6.8 Hz, ArH), 7.17 (t, 1H, J=7.3, Ar-H), 7.11 (s, 1H, Ar-H), 7.10 (d, 2H, J=7.3 Hz, Ar-H), 6.98 (s, 1H, ArH), 3.92 (s, 3H, Ar-OCH_3), 3.83 (s, 3H, Ar-OCH_3), 3.55–3.35 (m, 2H, CH_2CH_2OH), 3.00–2.85 [m, 1H, $ArC(CH_3)CH_aH_bCH_2OH$], 2.38–2.25 [m, 1H, $ArC(CH_3)CH_aH_bCH_2OH$], 1.72 [s, 3H, $ArC(CH_3)$] 1.65 (br, s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.0 (s, Ar-C), 147.7 (s, Ar-C), 147.5 (s, Ar-C), 137.7 (s, Ar-C), 128.1 (d, 2C, Ar-CH), 126.3 (d, 2C, Ar-CH), 125.5 (d, Ar-CH), 118.4 (d, Ar-CH), 114.2 (s, Ar-C), 112.6 (d, Ar-CH), 60.2 (t, CH_2CH_2OH), 56.2 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 46.3 [s, $ArC(CH_3)$], 41.8 (t, CH_2CH_2OH), 29.4 [q, $ArC(CH_3)$] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{21}BrO_3]^+$=$[M]^+$: 364.0669; found: 364.0659.



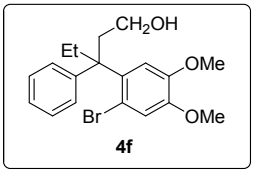
3-(2-bromo-3,4,5-trimethoxyphenyl)-3-phenylbutan-1-ol (**4d**): General procedure-3 was carried out with ester **3d** (212 mg, 0.50 mmol) in dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 40:60 to 30:70) furnished the title compound **4d** (179 mg, 94%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 60:40), R_f(**3d**)=0.65, R_f(**4d**)=0.20, UV detection].IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3398, 2922, 2851, 1564, 1483, 1446, 1380, 1321, 1164, 1103, 1050, 1010, 932, 819, 766, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, J=7.3 and 5.4 Hz, Ar-H), 7.17 (t, 1H, J=7.3 Hz, Ar-H), 7.11 (d, 2H, J=7.3 Hz, Ar-H), 6.99 (s, 1H, Ar-H), 3.93 (s, 3H, Ar-OCH_3), 3.90 (s, 3H, Ar-OCH_3), 3.79 (s, 3H, Ar-OCH_3), 3.50–3.35 (m, 2H, CH_2CH_2OH), 3.00–2.85 [m, 1H, $ArC(CH_3)CH_aH_bCH_2OH$], 2.40–2.25 [m, 1H, $ArC(CH_3)CH_aH_bCH_2OH$], 1.74 [s, 3H, $ArC(CH_3)$] 1.65 (br. s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.7 (s, Ar-C), 151.6 (s, Ar-C), 148.9 (s, Ar-C), 141.6 (s, Ar-C), 141.3 (s, Ar-C), 128.1 (d, 2C, Ar-CH), 126.1 (d, 2C, Ar-CH), 125.5 (d, Ar-CH), 111.4 (s, Ar-C), 108.8 (d, Ar-CH), 61.0 (q, Ar-OCH_3), 60.8 (q, Ar-OCH_3),

60.2 (t, CH_2OH), 56.2 (q, Ar-OCH_3), 47.1 [s, Ar*C*(CH_3)CH_2], 41.8 (t, *C*H_2CH_2OH) , 29.5 [q, ArC(*C*H_3)CH_2] ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{24}BrO_4]^+$=$[M+H]^+$: 395.0852; found: 395.0843.



4e

3-(2-bromo-4,5-dimethoxyphenyl)-3-(4-chlorophenyl)butan-1-ol (**4e**): General procedure-3 was carried out with ester **3e** (221 mg, 0.5 mmol) in dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 60:40 to 50:50) furnished the title compound **4e** (188 mg, 94%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3e**)=0.60, R_f(**4e**)=0.20, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3387, 2932, 2843, 1599, 1570, 1503, 1493, 1434, 1365, 1252, 1166, 1093, 1026, 1012, 827, 708, 631 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.22 (d, 2H, *J*=8.8 Hz, ArH), 7.10 (s, 1H, Ar-H), 7.04 (d, 2H, *J*=8.8 Hz, Ar-H), 6.99 (s, 1H, ArH), 3.93 (s, 3H, Ar-OCH_3), 3.84 (s, 3H, Ar-OCH_3), 3.35–3.55 (m, 2H, CH_2CH_2OH), 3.00–2.85 [m, 1H, ArC(CH_3)C$H_a$$H_b$$CH_2OH$], 2.35–2.20 [m, 1H, ArC(CH_3)$CH_a$$H_b$$CH_2OH$], 1.70 [s, 3H, ArC($CH_3$)], 1.65 (br. s, 1H, OH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.9 (s, Ar-C), 147.8 (s, Ar-C), 147.6 (s, Ar-C), 137.0 (s, Ar-C), 131.3 (s, Ar-C), 128.2 (d, 2C, Ar-CH), 127.8 (d, 2C, Ar-CH), 118.4 (d, Ar-CH), 114.1 (s, Ar-C), 112.6 (d, Ar-CH), 60.1 (t, CH_2OH), 56.2 (q, Ar-OCH_3), 56.1 (q, Ar-OCH_3), 46.0 [s, Ar*C*(CH_3)CH_2], 41.5 (t, *C*H_2CH_2OH), 29.6 [q, ArC(*C*H_3)CH_2] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{20}BrClO_3]^+$=$[M]^+$: 398.0279; found: 398.0283.



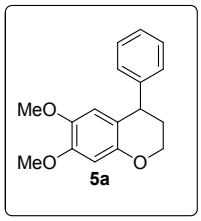
4f

3-(2-bromo-4,5-dimethoxyphenyl)-3-phenylpentan-1-ol (**4f**): General procedure-3 was carried out with ester **3f** (211 mg, 0.5 mmol) in dry ether, was added slowly $LiAlH_4$ (57 mg, 1.50 mmol) in portion wise 0 ˚C. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 50:50 to 40:60) furnished the title compound **4f** (174 mg, 92%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 60:40), R_f(**3f**)=0.80, R_f(**4f**)=0.40, UV detection].IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3365, 2960, 2930, 2849, 1569, 1502, 1462, 1440, 1315, 1248, 1209, 1161, 1026, 846, 791, 763, 734, 700, 621 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, *J*=7.8 and 5.4 Hz, ArH), 7.17 (t, 1H, *J*=7.3 Hz, Ar-H), 7.14 (s, 1H, Ar-H), 7.09 (d, 2H, *J*=7.3 Hz, Ar-H), 6.98 (s, 1H, Ar-H), 3.94 (s, 3H, Ar-OCH_3), 3.84 (s,

3H, Ar-OCH_3), 3.41 (t, 2H, *J*=7.3 Hz, CH_2CH_2OH), 2.85–2.70 [m, 1H, ArC(Et)C$H_aH_bCH_2OH$], 2.55–2.45 [m, 1H, ArC(Et)$CH_aH_bCH_2OH$], 2.40–2.25 [m, 1H, ArC(C$H_aH_bCH_3$)], 2.15–1.95 [m, 1H, ArC($CH_aH_bCH_3$)], 1.65 (br, s. 1H, OH), 1.23 (t, 2H, *J*=7.3 Hz, CH_2CH_2OH), 0.67 [t, 3H, *J*=7.3 Hz, ArC(CH_2CH_3)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.5 (s, Ar-C), 147.2 (s, Ar-C), 147.1 (s, Ar-C), 137.2 (s, Ar-C), 127.8 (d, 2C, Ar-CH), 127.4 (d, 2C, Ar-CH), 125.5 (d, Ar-CH), 118.5 (d, Ar-CH), 114.3 (s, Ar-C), 113.2 (d, Ar-CH), 59.9 (t, CH_2CH_2OH), 56.2 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 49.4 [s, ArC(Et)], 8.8 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{23}BrNaO_3]^+$=$[M+Na]^+$: 401.0723; found: 401.0723.

General Procedure-4 for the Synthesis of neo-flavans (5a-5f and 7am-7fe):

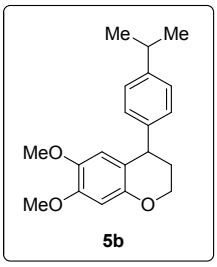
In an oven dried Schlenk tube under nitrogen atmosphere, were added alcohol **4 or 6** (0.30 mmol), CuI (20 mol%), 2,2'-Bipyridine (20 mol%), KO^{t}Bu (0.90 mmol), and followed by addition of DMF (3 mL). The resulted reaction mixture was stirred at 120 °C for 24 h. The reaction mixture was quenched by addition of aqueous NH_4Cl solution and then it was extracted with ethyl acetate (3 × 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue on a silica gel column chromatography using petroleum ether/ethyl acetate as eluent furnished neoflavan **5a-5f** (66-78%) and **7am-7fe** (69-95%).



5a

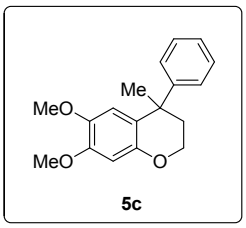
6,7-dimethoxy-4-phenylchromane (**5a**): General procedure-4 was carried out with alcohol **4a** (105 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **5a** (55 mg, 68%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**4a**)=0.15, R_f(**5a**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2853, 1507, 1465, 1452, 1380, 1264, 1217, 1196, 1132, 1024, 860, 733, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.30 (dd, 2H, *J*=7.3 and 7.3 Hz, Ar-H), 7.20 (t, 1H, *J*= 7.3 Hz, Ar-H), 7.14 (d, 2H, *J*=7.3 Hz, Ar-H), 6.44 (s, 1H, Ar-H), 6.31 (s, 1H, Ar-H), 4.17–4.07 [m, 3H, ArC*H*(Ph)CH_2 and ArOCH_2], 3.84 (s, 3H, $ArOCH_3$), 3.65 (s, 3H, Ar-OCH_3), 2.40–2.20 (m, 1H, $ArOCH_2CH_aH_b$), 2.10–1.90 (m, 1H, $ArOCH_2CH_aH_b$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.2 (s, Ar-C), 148.8 (s, Ar-C), 145.9 (s, Ar-C), 143.1 (s, Ar-C), 128.5 (d, 2C, Ar-CH), 128.4 (d, 2C, Ar-CH), 126.4 (d, Ar-CH), 114.6 (s, Ar-C), 113.0 (d, Ar-CH), 100.5 (d, Ar-CH), 63.5 (t,

ArO*C*H_2CH$_2$), 56.3 (q, Ar-OCH$_3$), 55.8 (q, Ar-OCH$_3$), 40.5 [d, Ar(Ph)*C*HCH$_2$], 32.0 (t, ArOCH$_2$*C*H$_2$) ppm. HR-MS (ESI+) m/z calculated for $[C_{17}H_{16}NaO_2]^+$=$[(M+Na)–H_2O]^+$: 275.1043; found: 275.1050.



5b

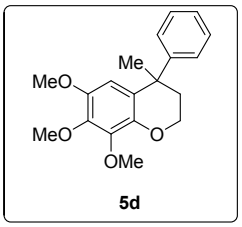
4-(4-isopropylphenyl)-6,7-dimethoxychromane (**5b**): General procedure-4 was carried out with alcohol **4b** (118 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 93:7) furnished the title compound **5b** (68 mg, 72%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**4b**)=0.10, R_f(**5b**)=0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2957, 2923, 2852, 1510, 1464, 1381, 1235, 1218, 1196, 1133, 1024, 830, 767, 665 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.15 (d, 2H, *J*=7.8 Hz, Ar-H), 7.04 (d, 2H, *J*=7.8 Hz, Ar-H), 6.43 (s, 1H, Ar-H), 6.34 (s, 1H, Ar-H), 4.15–3.95 [m, 3H, ArOCH_2 and ArC*H*(Ar)CH$_2$], 3.84 (s, 3H, Ar-OCH$_3$), 3.66 (s, 3H, Ar-OCH$_3$), 2.88 [sept, 1H, *J*=6.8 Hz, CH(CH$_3$)$_2$], 2.40–2.20 [m, 1H, ArCH(Ar)CH_aH$_b$], 2.10–1.90 [m, 1H, ArCH(Ar)CH$_a$$H_b$], 1.24 [d, 6H, *J*=6.8 Hz, CH(CH$_3$)$_2$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=149.2 (s, Ar-C), 148.7 (s, Ar-C), 146.9 (s, Ar-C), 143.2 (s, Ar-C), 143.1 (s, Ar-C), 128.4 (d, 2C, Ar-CH), 126.4 (d, 2C, Ar-CH), 114.8 (s, Ar-C), 113.2 (d, Ar-CH), 100.5 (d, Ar-CH), 63.5 (t, ArOCH$_2$), 56.4 (q, Ar-OCH$_3$), 55.8 (q, Ar-OCH$_3$), 40.0 (d, Ar*C*HCH$_2$), 33.6 [d, *C*H(CH$_3$)$_2$], 32.0 (t, ArOCH$_2$*C*H$_2$), 24.0 [q, 2C, 2 × CH(CH$_3$)] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{25}O_3]^+$=$[M+H]^+$: 313.1798; found: 313.1787.



5c

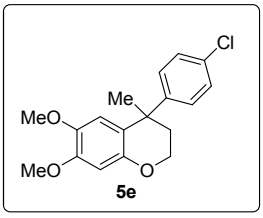
6,7-dimethoxy-4-methyl-4-phenylchromane (**5c**): General procedure-4 was carried out with alcohol **4c** (109 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished

the title compound **5c** (56 mg, 66%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**4c**)=0.30, R_f(**5c**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2959, 2925, 1505, 1215, 1192, 1127, 1101, 1080, 1051, 969, 906, 877, 729cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.27 (dd, 2H, *J*=7.8 and 7.8 Hz, Ar-H), 7.22–7.13 (m, 3H, Ar-H), 6.51 (s, 1H, Ar-H), 6.44 (s, 1H, Ar-H), 4.14–4.02 (m, 1H, $ArOCH_aH_bCH_2$), 3.92–3.80 (m, 1H, $ArOCH_aH_bCH_2$), 3.86 (s, 3H, Ar-OCH_3), 3.72 (s, 3H, Ar-OCH_3), 2.18–2.02 (m, 2H, $ArOCH_2CH_2$), 1.76 [s, 3H, $ArCCH_3$(Ph)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.8 (s, Ar-C), 148.6 (s, Ar-C), 148.5 (s, Ar-C), 143.1 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 127.3 (d, 2C, Ar-CH), 125.9 (d, Ar-CH), 119.6 (s, Ar-C), 111.6 (d, Ar-CH), 100.5 (d, Ar-CH), 62.8 (t, $ArOCH_2CH_2$), 56.4 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 39.8 (t, $ArOCH_2CH_2$), 39.1 [s, $ArC(CH_3)$(Ph)], 29.3 [s, $ArC(CH_3)$(Ph)] ppm. HR-MS (ESI+) m/z calculated for $[C_{18}H_{18}KO_2]^+$=$[(M+K)–H_2O]^+$: 305.0938; found: 305.0931.

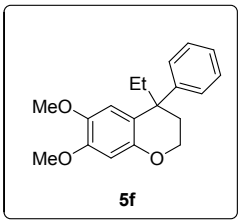


5d

6,7,8-trimethoxy-4-methyl-4-phenylchromane (**5d**): General procedure-4 was carried out with alcohol **4d** (118 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the title compound **5d** (63 mg, 67%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 60:40), R_f(**4d**)=0.20, R_f(**5d**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2852, 1491, 1451, 1416, 1340, 1274, 1198, 1118, 1084, 1070, 927, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.27 (dd, 2H, *J*=7.3 and 7.3 Hz, Ar-H), 7.16 (m, 3H, Ar-H), 6.30 (s, 1H, Ar-H), 4.10–4.25 [m, 1H, $ArOCH_aH_b$], 3.95–3.85 [m, 1H, $ArOCH_aH_b$], 3.93 (s, 3H, Ar-OCH_3), 3.92 (s, 3H, Ar-OCH_3), 3.68 (s, 3H, Ar-OCH_3), 2.20–2.00 (m, 2H, $ArOCH_2CH_2$), 1.75 [s, 3H, $ArC(Ph)CH_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.5 (s, Ar-C), 146.6 (s, Ar-C), 142.6 (s, Ar-C), 142.0 (s, Ar-C), 141.6 (s, Ar-C), 128.0 (d, 2H, Ar-CH), 127.3 (d, 2H, Ar-CH), 126.0 (d, Ar-CH), 124.1 (s, Ar-C), 106.7 (d, Ar-CH), 62.9 (t, $ArOCH_2CH_2$), 61.3 (q, Ar-OCH_3), 61.2 (q, Ar-OCH_3),56.4 (q, Ar-OCH_3), 39.7 (t, $ArOCH_2CH_2$), 39.5 [s, $ArC(Ph)CH_3$], 29.4 (q, $ArC(Ph)CH_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{23}O_4]^+$=$[M+H]^+$: 315.1591; found: 315.1582.



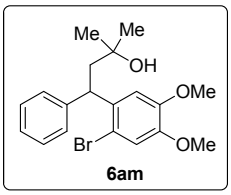
4-(4-chlorophenyl)-6,7-dimethoxy-4-methylchromane (**5e**): General procedure-4 was carried out with alcohol **4e** (120 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the title compound **5e** (69 mg, 72%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 90:10), R_f(**4e**)=0.10, R_f(**5e**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2934, 2831, 1505, 1442, 1403, 1266, 1253, 1204, 1161, 1101, 1053, 1010, 907, 826, 730 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.22 (d, 2H, J=8.3 Hz, Ar-H), 7.09 (d, 2H, J=8.3 Hz, Ar-H), 6.44 (s, 1H, Ar-H), 6.42 (s, 1H, Ar-H), 4.00–4.20 [m, 1H, ArOCH_aH$_b$CH$_2$], 3.90–3.77 [m, 1H, ArOCH$_a$$H_b$], 3.84 (s, 3H, Ar-OCH$_3$), 3.71 (s, 3H, Ar-OCH$_3$), 2.20–1.95 (m, 2H, ArOCH$_2$CH_2), 1.72 [s, 3H, ArC(Ar)CH_3] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.8 (s, Ar-C), 148.5 (s, Ar-C), 148.4 (s, Ar-C), 143.3 (s, Ar-C), 131.8 (s, Ar-C), 128.8 (d, 2C, Ar-CH), 128.1 (d, 2C, Ar-CH), 119.1 (s, Ar-C), 111.4 (d, Ar-CH), 100.6 (d, Ar-CH), 62.8 (t, ArOCH$_2$CH$_2$), 56.5 (q, Ar-OCH$_3$), 55.8 (q, Ar-OCH$_3$), 39.8 (t, ArOCH$_2$$CH_2$), 38.9 [s, Ar$C$(Ar)(CH$_3$)], 29.3 [q, ArC(Ar)($CH_3$)] ppm. HR-MS (ESI+) m/z calculated for [$C_{18}H_{20}ClO_3$]$^+$=[M+H]$^+$: 319.1095; found: 319.1087.



4-ethyl-6,7-dimethoxy-4-phenylchromane (**5f**): General procedure-4 was carried out with alcohol **4f** (114 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu(101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 90:10) furnished the title compound **5f** (70 mg, 78%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**4f**)=0.20, R_f(**5f**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2959, 2924, 2852, 1506, 1442, 1266, 1246, 1197, 1160, 1043, 924, 831, 789, 761, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.25 (dd, 2H, J=7.8 and 7.3 Hz, Ar-H), 7.17 (m, 3H, Ar-H), 6.53 (s, 1H, Ar-H), 6.43 (s, 1H, Ar-H), 4.00–4.25 [m, 1H, ArOCH_aH$_b$], 3.86 (s, 3H, Ar-OCH$_3$), 3.85–3.70 [m, 1H, ArOCH$_a$$H_b$], 3.75 (s, 3H, Ar-OCH$_3$), 2.45–2.30 (m, 1H, ArOCH$_2$CH_aH$_b$), 2.28–2.18 (m, 1H, ArOCH$_2$CH$_a$$H_b$), 2.17–2.05 (m, 1H, C$H_aH_bCH_3$), 1.85–2.00 (m, 1H, CH$_a$$H_bCH_3$), 0.85 (t, 3H, J=7.3 Hz, CH$_2$CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz):

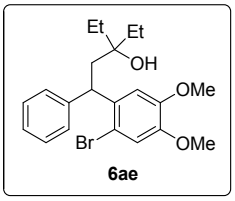
δ=150.1 (s, Ar-C), 149.9 (s, Ar-C), 148.6 (s, Ar-C), 143.0 (s, Ar-C), 128.0 (d, 2C, Ar-C), 127.5 (d, 2C, Ar-C), 125.9 (d, Ar-CH), 116.1 (s, Ar-C), 111.9 (d, Ar-CH), 100.6 (d, Ar-CH), 62.6 (t, $ArOCH_2$), 56.5 (q, Ar-OCH_3), 55.6 (q, Ar-OCH_3), 43.3 [s, ArC(Ph)Et], 34.6 (t, $ArOCH_2CH_2$), 32.8 (t, CH_2CH_3), 9.3 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{23}O_3]^+$=$[M+H]^+$: 299.1642; found: 299.1637.

General Procedure-5 for the synthesis of tertiary alcohol (6am-6fe): To a cold (–10 °C), magnetically stirred ester **3a-3f** (0.50 mmol) in 5 mL of dry ether, was added methylmagnesium bromide (4.00 mmol) or ethylmagnesium bromide (4.00 mmol) [prepared from magnesium (4.00 mmol) and methyl iodide (8.00 mmol) or ethyl bromide (8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether] at –10 °C. The reaction mixture was stirred at RT for 4 h. It was then poured into a cold saturated aqueous NH_4Cl solution and then aqueous layer was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. Purification of the residue by silica gel column chromatography, furnished the tertiary alcohol **6am-6fe** (70–92%).

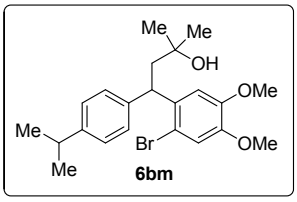


6am

4-(2-bromo-4,5-dimethoxyphenyl)-2-methyl-4-phenylbutan-2-ol (**6am**): General procedure-5 was carried out with ester **3a** (196 mg, 0.50 mmol), methylmagnesium iodide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25 to 70:30) furnished the alcohol **6am** (136 mg, 72%) as pale yellow viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3a**)=0.45, R_f(**6am**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3432, 2959, 2924, 1572, 1505, 1439, 1377, 1240, 1209, 844 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.36 (d, 2H, J=7.3 Hz, Ar-H), 7.28 (dd, 2H, J=8.3 and J=7.3 Hz, Ar-H), 7.18 (t, 1H, J=7.3 Hz, Ar-H), 6.98 (s, 1H, Ar-H), 6.84 (s, 1H, Ar-H), 4.71 (t, 1H, J=7.3 Hz, $ArCHCH_2$), 3.81 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, Ar-OCH_3), 2.40–2.20 (m, 2H, $ArCHCH_2$), 1.20 [s, 3H, $CH(CH_3)_2OH$], 1.19 [s, 3H, $CH(CH_3)_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.6 (s, Ar-C), 147.9 (s, Ar-C), 144.5 (s, Ar-C), 136.3 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 127.7 (d, 2C, Ar-CH), 126.4 (d, Ar-CH), 115.5 (d, Ar-CH), 114.1 (s, Ar-C), 111.5 (d, Ar-CH), 71.4 [s, $C(CH_3)_2OH$], 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 48.7 (t, $ArCHCH_2$), 44.9 (d, $ArCHCH_2$), 30.1 (q, CH_3), 29.9 (q, CH_3)ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{23}BrKO_3]^+$=$[M+K]^+$: 417.0462; found: 417.0465.

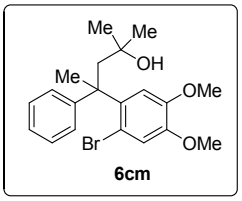


1-(2-bromo-4,5-dimethoxyphenyl)-3-ethyl-1-phenylpentan-3-ol (**6ae**): General procedure-5 was carried out with ester **3a** (196 mg, 0.50 mmol), ethylmagnesium bromide (4.00 mmol [prepared from magnesium (96 mg, 4.00 mmol), ethyl iodide (0.59 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25) furnished the alcohol **6ae** (142 mg, 70%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**3a**)=0.60, R_f(**6ae**)=0.50, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3454, 3026, 2962, 2922, 2850, 1500, 1461, 1377, 1259, 1200, 1159, 1028, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.37 (d, 2H, *J*=7.3 Hz, Ar-H), 7.27 (dd, 2H, *J*=7.3 and 7.3 Hz, Ar-H), 7.16 (t, 1H, *J*=7.3 Hz, Ar-H), 6.97 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 4.69 (t, 1H, *J*=6.3 Hz, ArC*H*CH_2), 3.84 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, Ar-OCH_3), 2.40–2.15 (m, 2H, ArCHC*H*$_2$), 1.55–1.4 [m, 4H, C(C*H*$_2$$CH_3$)$_2$], 6.81 [q, 6H, *J*=7.3 Hz, C(CH_2C*H*$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.6 (s, Ar-C), 147.9 (s, Ar-C), 144.9 (s, Ar-C), 136.5 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 127.7 (d, 2C, Ar-CH), 126.4 (d, Ar-CH), 115.5 (d, Ar-CH), 114.2 (s, Ar-C), 111.7 (d, Ar-CH), 75.3 [s, *C*(Et)$_2$OH], 56.1 (q, Ar-OCH_3), 56.1 (q, Ar-OCH_3), 44.1 (d, Ar*C*HCH_2), 43.9 (t, ArCH*C*H_2), 31.4 (t, CH_2CH_3), 31.1 (t, CH_2CH_3), 7.9 [q, 2C, C(CH_2*C*H_3)$_2$OH] ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{27}BrNaO_3]^+$=$[M+Na]^+$: 429.1036; found: 429.1021.

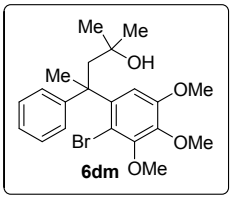


4-(2-bromo-4,5-dimethoxyphenyl)-4-(4-isopropylphenyl)-2-methylbutan-2-ol (**6bm**): General procedure-5 was carried out with ester **3b** (217 mg, 0.50 mmol), methylmagnesium iodide (4.00 mmol), [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25) furnished the alcohol **6bm** (165 mg, 78%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3b**)=0.50, R_f(**6bm**)=0.35, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3432, 2959, 2924, 1572, 1505, 1439, 1377, 1240, 1209, 844 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.28 (d, 2H, *J*=7.8 Hz, Ar-H), 7.13 (d, 2H, *J*=7.8 Hz, Ar-H), 6.97 (s, 1H, Ar-H), 6.86 (s, 1H, Ar-H), 4.68 (t, 1H, *J*=6.8 Hz, ArC*H*CH_2), 3.82 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, Ar-OCH_3), 2.84 [sept, 1H, *J*=6.8 Hz, C*H*(CH_3)$_2$], 2.40–2.20 (m, 2H, ArCHCH_2), 1.21 [s, 6H, CH(CH_3)$_2$OH],

1.19 [d, 6H, J=6.8 Hz, CH(CH_3)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.6 (s, Ar-C), 147.9 (s, Ar-C), 146.9 (s, Ar-C), 141.7 (s, Ar-C), 136.5 (s, Ar-C), 127.5 (d, 2C, Ar-CH), 126.6 (d, 2C, Ar-CH), 115.5 (d, Ar-CH), 114.1 (s, Ar-C), 111.5 (d, Ar-CH), 71.5 [s, $CH_2C(CH_3)_2OH$], 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 48.8 (t, ArCHCH_2), 44.5 (d, Ar$CHCH_2$), 33.6 [d, $CH(CH_3)_2$], 30.1 [q, CH(CH_3)$_a$(CH_3)$_b$], 29.7 [q, CH(CH_3)$_a$(CH_3)$_b$], 23.9 [s, 2C, $CH(CH_3)_2$] ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{29}BrNaO_3]^+$=$[M+Na]^+$: 443.1192; found: 443.1180.

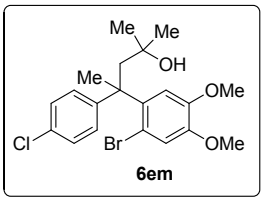


4-(2-bromo-4,5-dimethoxyphenyl)-2-methyl-4-phenylpentan-2-ol (**6cm**): General procedure-5 was carried out with ester **3c** (203 mg, 0.50 mmol), methylmagnesium iodide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 70:30) furnished the alcohol **6cm** (177 mg, 90%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3c**)=0.75, R_f(**6cm**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3055, 2969, 2841, 1503, 1441, 1317, 1252, 1172, 1029, 767, 731, 698 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.27 (s, 1H, Ar-H), 7.24 (d, 2H, J=7.8 Hz, Ar-H), 7.13 (m, 3H, Ar-H), 6.97 (s, 1H, Ar-H), 3.95 (s, 3H, Ar-OCH_3), 3.84 (s, 3H, Ar-OCH_3), 3.21 [d, 1H, J=14.2 Hz, ArC(Me)CH_aH$_b$], 2.34 [d, 1H, J=14.2 Hz, ArC(Me)CH$_a$$H_b$], 1.85 [s, 3H, ArC(C$H_3$)$_a$($CH_3$)$_b$], 1.20 [s, 3H, ArC($CH_3$)$_a$(C$H_3$)$_b$], 0.98 [s, 3H, ArC($CH_3$)$CH_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.6 (s, Ar-C), 147.8 (s, Ar-C), 147.5 (s, Ar-C), 137.5 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 125.9 (d, 2C, Ar-CH), 125.3 (d, Ar-C), 118.1 (d, Ar-C), 115.4 (s, Ar-C), 113.6 (d, Ar-C), 72.3 [s, $CH_2C(CH_3)_2OH$], 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 47.8 [t, $CH_2C(CH_3)_2OH$], 47.1 [s, Ar$C(CH_3)CH_2$], 33.0 [q, $CH_2C(CH_3)_a(CH_3)_bOH$], 32.9 [q, $CH_2C(CH_3)_a(CH_3)_bOH$], 30.3 [q, ArC(CH_3)] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{24}BrO_2]^+$=$[(M+H)–H_2O]^+$: 375.0954; found: 375.0936.



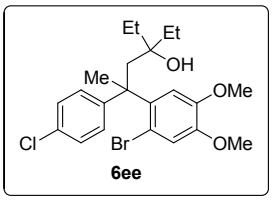
4-(2-bromo-3,4,5-trimethoxyphenyl)-2-methyl-4-phenylpentan-2-ol (**6dm**): General procedure-5 was carried out with ester **3d** (218 mg, 0.50 mmol), methylmagnesium iodide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and

a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 70:30) furnished the alcohol **6dm** (161 mg, 76%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3d**)=0.40, R_f(**6dm**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3428, 3056, 2963, 2923, 1483, 1463, 1381, 1318, 1162, 1103, 1008, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.23 (dd, 2H, *J*=8.3 and 7.8 Hz, Ar-H), 7.18–7.05 (m, 4H, Ar-H), 3.93 (s, 3H, Ar-OCH_3), 3.91 (s, 3H, Ar-OCH_3), 3.76 (s, 3H, Ar-OCH_3), 3.26 [d, 1H, *J*=14.2 Hz, ArC(CH_3)C$H_a$$H_b$)], 2.33 [d, 1H, *J*=14.2 Hz, ArC(CH_3)C$H_a$$H_b$)], 1.84 [s, 3H, ArC($CH_3$)], 1.18 [s, 3H, C($CH_3$)$_a$($CH_3$)$_b$], 0.94 [s, 3H, C($CH_3$)$_a$($CH_3$)$_b$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=151.8 (s, Ar-C), 151.7 (s, Ar-C), 151.6 (s, Ar-C), 141.9 (s, Ar-C), 141.2 (s, Ar-C), 128.1 (d, 2C, Ar-CH), 125.8 (d, 2C, Ar-CH), 125.3 (d, Ar-CH), 112.8 (s, Ar-C), 110.0 (d, Ar-CH) , 72.4 [s, *C*(CH_3)$_2$OH], 61.2 (q, Ar-OCH_3), 60.8 (q, Ar-OCH_3), 56.3 (q, Ar-OCH_3), 48.0 [s, Ar*C*(CH_3)CH_2], 47.8 [t, ArC(CH_3)*C*H_2], 33.4 [q, CH_2C(*C*H_3)$_a$(CH_3)$_b$OH], 33.1 [q, CH_2C(CH_3)$_a$(*C*H_3)$_b$OH], 30.1 [q, ArC(*C*H_3)CH_2]ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{27}BrNaO_4]^+$=$[M+Na]^+$: 445.0985; found: 445.0971.

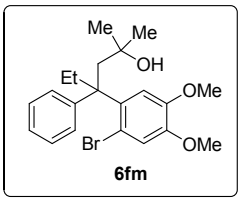


6em

4-(2-bromo-4,5-dimethoxyphenyl)-4-(4-chlorophenyl)-2-methylpentan-2-ol (**6em**): General procedure-5 was carried out with ester **3e** (220 mg, 0.50 mmol), methylmagnesium iodide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25) furnished the alcohol **6em** (165 mg, 77%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3e**)=0.60, R_f(**6em**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3434, 2965, 2929, 1503, 1439, 1251, 1210, 1171, 1094, 1011, 909, 728 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.23 (s, 1H, Ar-H), 7.18 (d, 2H, *J*=8.8 Hz, Ar-H), 7.03 (d, 2H, *J*=8.8 Hz, Ar-H), 6.95 (s, 1H, Ar-H), 3.93 (s, 3H, Ar-OCH_3), 3.84 (s, 3H, Ar-OCH_3), 3.16 [d, 1H, *J*=14.2 Hz, ArC(Me)C$H_a$$H_b$], 2.26 [d, 1H, *J*=14.2 Hz, ArC(Me)C$H_a$$H_b$], 1.80 [s, 3H, ArC(C$H_3$)$_a$($CH_3$)$_b$], 1.18 [s, 3H, ArC($CH_3$)$_a$(C$H_3$)$_b$], 0.93 [s, 3H, ArC(*C*$H_3$)$CH_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=150.4 (s, Ar-C), 148.0 (s, Ar-C), 147.6 (s, Ar-C), 136.9 (s, Ar-C), 131.0 (s, Ar-C), 128.1 (d, 2C, Ar-CH), 127.4 (d, 2C, Ar-CH), 118.1 (d, Ar-CH), 115.3 (s, Ar-C), 113.5 (d, Ar-CH), 72.3 [s, CH_2*C*(CH_3)$_2$OH], 56.2 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 47.6 [t, *C*H_2C(CH_3)$_2$OH], 46.8 [s, Ar*C*(CH_3)CH_2], 33.2 [q, CH_2*C*(*C*H_3)$_a$(CH_3)$_b$OH], 33.1 [q, CH_2*C*(CH_3)$_a$(*C*H_3)$_b$OH], 30.2 [q, ArC(*C*H_3)] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{24}BrClNaO_3]^+$=$[M+Na]^+$: 449.0490; found: 449.0478.

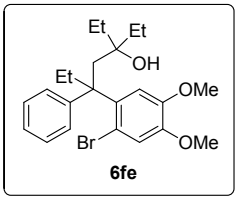


5-(2-bromo-4,5-dimethoxyphenyl)-5-(4-chlorophenyl)-3-ethylhexan-3-ol (**6ee**): General procedure-5 was carried out with ester **3e** (220 mg, 0.5 mmol), ethylmagnesium bromide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), ethyl bromide (0.59 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25) furnished the alcohol **6ee** (180 mg, 79%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3e**)=0.60, R_f(**6ee**)=0.50, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3400, 2963, 2924, 1503, 1439, 1316, 1250, 1168, 1011, 826, 736 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.24 (s, 1H, Ar-H), 7.17 (d, 2H, J=8.8 Hz, Ar-H), 7.03 (d, 2H, J=8.8 Hz, Ar-H), 6.95 (s, 1H, Ar-H), 3.92 (s, 3H, Ar-OCH_3), 3.83 (s, 3H, Ar-OCH_3), 3.09 [d, 1H, J=14.2 Hz, ArC(CH_3)C$H_a$$H_b$)], 2.20 [d, 1H, J=14.2 Hz, ArC(CH_3)C$H_a$$H_b$)], 1.82 [s, 3H, ArC(C$H_3$)], 1.50 (q, 2H, J=7.3 Hz, C$H_2$$CH_3$), 1.30–1.10 (m, 2H, C$H_2$$CH_3$), 0.89 (br. s, 1H, OH), 0.86 (t, 3H, J=7.3 Hz, $CH_2$$CH_3$), 0.71 (t, 3H, J=7.3 Hz, $CH_2$$CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=150.5 (s, Ar-C), 147.9 (s, Ar-C), 147.5 (s, Ar-C), 137.4 (s, Ar-C), 130.9 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 127.4 (d, 2C, Ar-CH), 118.1 (d, Ar-CH), 115.2 (s, Ar-C), 113.5 (d, Ar-CH), 76.1 [s, *C*(Et)$_2$OH], 56.1 (q, Ar-OCH_3), 56.0 (q, Ar-OCH_3), 46.8 (s, Ar*C*(CH_3)CH_2], 42.9 [t, *C*H_2C(Et)$_2$OH)], 33.4 (t, *C*$H_2$$CH_3$), 33.2 (q, ArC(*C*$H_3$)$CH_2$), 31.8 (t, *C*$H_2$$CH_3$), 8.1 (q, CH_2*C*H_3), 8.0 (q, CH_2*C*H_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{28}BrClNaO_3]^+$=$[M+Na]^+$: 477.0803; found: 477.0785.



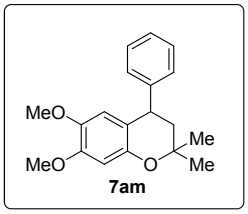
5-(2-bromo-4,5-dimethoxyphenyl)-3-ethyl-5-phenylhexan-3-ol (**6fm**): General procedure-5 was carried out with ester **3f** (210 mg, 0.5 mmol), methylmagnesium iodide (4.00 mmol) [prepared from magnesium (96 mg, 4.00 mmol), methyl iodide (0.51 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 75:25) furnished the alcohol **6fm** (187 mg, 92%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3f**)=0.60, R_f(**6fm**)=0.45, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3537, 2963, 2930, 1568, 1501, 1440, 1247, 1168, 1029, 761, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.55–7.05 (m, 5H, Ar-H), 6.95 (s, 2H, Ar-H), 3.94 (s, 3H, Ar-OCH_3), 3.83 (s, 3H, Ar-OCH_3), 2.97 [d, 1H, J=14.7 Hz, ArC(Et)C$H_a$$H_b$], 2.80–2.65 [m, 1H, ArC(C$H_a$$H_b$$CH_3$)], 2.42 [d, 1H, J=14.7 Hz,

ArC(Et)CH_aH_b], 2.03 (br, s, 1H, OH), 1.16 [s, 3H, ArC(CH_3)$_a$(CH_3)$_b$], 0.95 [s, 3H, ArC(CH_3)$_a$(CH_3)$_b$], 0.66 [t, 3H, *J*=7.3 Hz, ArC(CH_2CH_3)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.3 (s, Ar-C), 147.6 (s, Ar-C), 147.4 (s, Ar-C), 138.1 (s, Ar-C), 127.4 (d, 2C, Ar-CH), 125.3 (d, 2C, Ar-CH), 118.4 (d, 2C, Ar-CH), 115.6 (s, Ar-C), 113.7 (d, Ar-CH), 72.3 [s, $CH_2C(CH_3)_2OH$], 56.2 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 49.8 [s, Ar*C*(Et)CH_2], 32.9 [q, C(CH_3)$_a$(CH_3)$_b$OH], 30.4 [q, C(CH_3)$_a$(CH_3)$_b$OH], 9.1 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{27}BrNaO]^+$=$[M+Na]^+$: 429.1036; found: 429.1033.



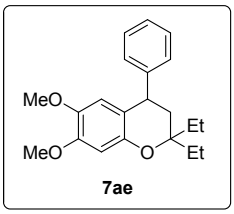
6fe

5-(2-bromo-4,5-dimethoxyphenyl)-3-ethyl-5-phenylheptan-3-ol (**6fe**): General procedure-5 was carried out with ester **3f** (210 mg, 0.50 mmol) ethylmagnesium bromide (4.00 mmol), [prepared from magnesium (96 mg, 4.00 mmol), ethyl bromide (0.59 mL, 8.00 mmol) and a catalytic amount of iodine in 20 mL of dry ether]. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 70:30) furnished the alcohol **6fe** (154 mg, 71%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**3f**)=0.60, R_f(**6fe**)=0.50, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3420, 2964, 2932, 2850, 1502, 1441, 1364, 1248, 1164, 1030, 760, 701 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.33 (s, 1H, Ar-H), 7.30–7.00 (m, 5H, Ar-H), 6.94 (s, 1H, Ar-H), 3.94 (s, 3H, Ar-OCH_3), 3.83 (s, 3H, Ar-OCH_3), 2.89 [d, 1H, *J*=14.7 Hz, ArC(Me)CH_aH_b], 2.83–2.70 [m, 1H, ArC(C$H_aH_bCH_3$)], 2.34 [d, 1H, *J*=14.7 Hz, ArC(Me)CH_aH_b], 2.15–2.00 [br. s, 1H, OH], 1.60–1.35 [m, 2H, $CH_2C(CH_2CH_3)_a(CH_2CH_3)_b$], 1.20–1.00 [m, 2H, $CH_2C(CH_2CH_3)_a(CH_2CH_3)_b$], 0.85 [t, 3H, *J*=7.3 Hz, ArC(CH_2CH_3)$_a$(CH_2CH_3)$_b$], 0.71 [t, 3H, *J*=7.3 Hz, ArC(CH_2CH_3)$_a$(CH_2CH_3)$_b$], 0.65 [t, 3H, *J*=7.3 Hz, ArC(CH_2CH_3)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.5 (s, Ar-C), 147.6 (s, Ar-C), 147.3 (s, Ar-C), 138.6 (s, Ar-C), 129.0 (d, 2C, Ar-CH), 128.2 (d, 2C, Ar-CH), 127.5 (d, Ar-CH), 118.3 (d, Ar-CH), 115.5 (s, Ar-C), 113.9 (d, Ar-CH), 76.2 [s, $CH_2C(CH_3)_2OH$], 56.2 (q, Ar-OCH_3), 55.9 (q, Ar-OCH_3), 49.9 [s, Ar*C*(Et)CH_2], 33.4 (t, *C*H_2CH_3), 31.8 (t, *C*H_2CH_3), 9.3 (q, CH_2CH_3), 8.2 (q, CH_2CH_3), 8.1 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{31}BrNaO_3]^+$=$[M+Na]^+$: 457.1349; found: 457.1338.



7am

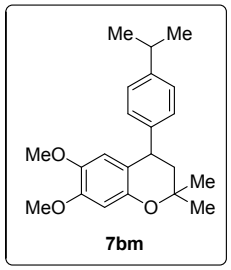
6,7-dimethoxy-2,2-dimethyl-4-phenylchromane (**7am**): General procedure-4 was carried out with alcohol **6am** (113 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **7am** (62 mg, 69%) as colorless viscous liquid [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6am**)=0.30, R_f(**7am**)=0.60, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2972, 2932, 2851, 1503, 1441, 1383, 1261, 1237, 1193, 1121, 1012, 914, 824, 726, 699 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.31 (dd, 2H, J=7.8 and 6.8 Hz, Ar-H), 7.27–7.22 (m, 1H, Ar-H), 7.19 (dd, 2H, J=6.8 and 1.5 Hz, Ar-H), 6.42 (s, 1H, Ar-H), 6.22 (s, 1H, Ar-H), 4.00–3.97 [m, 1H, ArC*H*(Ph)], 3.83 (s, 3H, Ar-OCH_3), 3.58 (s, 3H, Ar-OCH_3), 2.10–1.80 [m, 2H, ArOC$(CH_3)_2$CH_2], 1.42 [s, 3H, ArOC(CH_3)$_a$(CH_3)$_b$], 1.35 [s, 3H, ArOC(CH_3)$_a$(CH_3)$_b$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.8 (s, Ar-C), 148.1 (s, Ar-C), 145.2 (s, Ar-C), 142.7 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.5 (d, 2C, Ar-CH), 126.5 (d, Ar-CH), 114.8 (s, Ar-C), 112.6 (d, Ar-CH), 101.0 (d, Ar-CH), 74.5 [q, ArO*C*(CH_3)$_a$(CH_3)$_b$], 56.4 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 44.0 (t, ArOC$(CH_3)_2$*C*H_2), 39.7 [d, Ar*C*H(Ph)CH_2], 29.8 [q, ArOC(*C*H_3)$_a$(CH_3)$_b$], 23.9 [q, ArOC(CH_3)$_a$(*C*H_3)$_b$] ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{23}O_3]^+$=$[M+H]^+$: 299.1642; found: 299.1635.



7ae

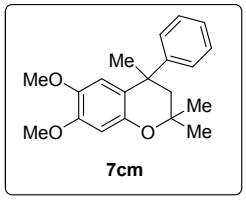
2,2-diethyl-6,7-dimethoxy-4-phenylchromane (**7ae**): General procedure-4 was carried out with alcohol **6ae** (122 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **7ae** (68 mg, 70%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 70:30), R_f(**6ae**)=0.50, R_f(**7ae**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2958, 2919, 2850, 1504, 1462, 1378, 1199, 1124, 1008, 922, 830, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.31 (dd, 2H, J=7.3 and 7.3 Hz, Ar-H), 7.26–7.16 (m, 3H, Ar-H), 6.42 (s, 1H, Ar-H), 6.20 (s, 1H, Ar-H), 4.05–3.90 [m, 1H, ArCH(Ph)], 3.83 (s, 3H, Ar-OCH_3), 3.57 (s, 3H, Ar-OCH_3), 2.05–1.97 [m, 1H, ArOC$(Et)_2CH_aH_b$], 1.95–1.50 [m, 5H, ArOC$(Et)_2CH_aH_b$ and ArOC$(CH_3CH_2)_2$], 0.94 [t, 3H, J=7.3 Hz, ArOC$(CH_2CH_3)_a(Et)_b$], 0.91 [t, 3H, J=7.3 Hz, ArOC$(Et)_a(CH_2CH_3)_b$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.8 (s, Ar-C), 148.2 (s, Ar-C), 145.4 (s, Ar-C), 142.5 (s, Ar-C), 128.6 (d, 2C, Ar-CH), 128.5 (d, 2C, Ar-CH), 126.5 (d, Ar-CH), 115.2 (s, Ar-C), 112.5 (d, Ar-CH), 101.0 (d, Ar-CH), 78.8[s, ArO*C*$(Et)_2$], 56.4 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 39.6 [t, ArOC$(Et)_2$*C*H_2], 39.0 [s, Ar*C*(Ph)CH_2], 30.7 (q,

CH_2CH$_3$), 25.8 (t, *C*H_2CH$_3$), 7.7 (q, CH$_2$*C*H$_3$), 7.5 (q, CH$_2$*C*H$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{26}NaO_3]^+$=$[M+Na]^+$: 349.1774; found: 349.1766.



7bm

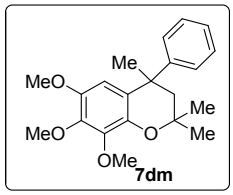
4-(4-isopropylphenyl)-6,7-dimethoxy-2,2-dimethylchromane (**7bm**): General procedure-4 was carried out with alcohol **6bm** (126 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **7bm** (77 mg, 75%) as white solid, recrystallized the solid in dichloromethane/hexane, m. p. 90–93 ˚C. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6bm**)=0.35, R_f(**7bm**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2956, 2922, 2851, 1510, 1464, 1382, 1238, 1195, 1124, 1017, 834, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.16 (d, 2H, *J*=8.3 Hz, Ar-H), 7.09 (d, 2H, *J*=8.3 Hz, Ar-H), 6.40 (s, 1H, Ar-H), 6.25 (s, 1H, Ar-H), 4.00–3.90 [m, 1H, ArC*H*(Ar)CH$_2$], 3.82 (s, 3H, Ar-OCH$_3$), 3.59 (s, 3H, Ar-OCH$_3$), 2.89 [sept, 1H, *J*=7.8 Hz, CH(CH$_3$)$_2$], 2.10–1.80 [m, 2H, ArCH(Ar)C*H*$_2$], 1.40 [s, 3H, ArOC(C*H*$_3$)$_a$(CH$_3$)$_b$], 1.33 [s, 3H, ArOC(CH$_3$)$_a$(C*H*$_3$)$_b$], 1.25 [d, 6H, *J*=7.8 Hz, CH(CH$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=148.8 (s, Ar-C), 148.1 (s, Ar-C), 147.0 (s, Ar-C), 142.6 (s, Ar-C), 142.3 (s, Ar-C), 128.4 (d, 2C, Ar-CH), 126.5 (d, 2C, Ar-CH), 115.0 (s, Ar-C), 112.8 (d, Ar-CH), 100.9 (d, Ar-CH), 74.5 [s, ArO*C*(CH$_3$)$_2$], 56.5 (q, Ar-OCH$_3$), 55.5 (q, Ar-OCH$_3$), 44.1 [t, ArOC(CH$_3$)$_2$*C*H$_2$], 39.2 [s, Ar*C*H(Ar)], 33.7 [d, CH(CH$_3$)$_2$], 29.8 [q, ArOC(*C*H$_3$)$_a$(CH$_3$)$_b$], 24.0 [q, ArOC(CH$_3$)$_a$(*C*H$_3$)$_b$], 23.9 [q, 2C, CH(*C*H$_3$)$_2$] ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{29}O_3]^+$=$[M+H]^+$: 341.2111; found: 341.2100.



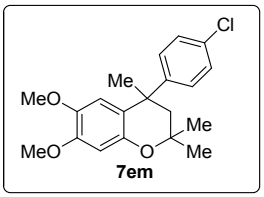
7cm

6,7-dimethoxy-2,2,4-trimethyl-4-phenylchromane (**7cm**): General procedure-4 was carried out with alcohol **6cm** (117 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚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 title compound **7cm** (72 mg, 77%) as colorless viscous liquid. [TLC control

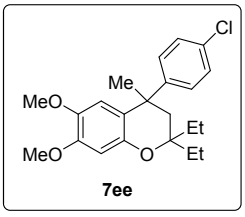
(petroleum ether/ethyl acetate, 80:20), R_f(**6cm**)=0.50, R_f(**7cm**)=0.75, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3056, 2969, 2930, 1507, 1444, 1255, 1209, 1196, 1161, 1112, 1041, 1009, 919, 828, 722 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.30–7.05 (m, 5H, Ar-H), 6.66 (s, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 3.86 (s, 3H, Ar-OCH_3), 3.77 (s, 3H, Ar-OCH_3) 2.34 [d, 1H, J=14.2 Hz, $ArOC(CH_3)_2CH_aH_b$], 2.05 [d, 1H, J=14.2 Hz, $ArOC(CH_3)_2CH_aH_b$], 1.68 [s, 3H, $ArOC(CH_3)_a(CH_3)_b$], 1.33 [s, 3H, $ArOC(CH_3)_a(CH_3)_b$], 0.87 [s, 3H,$ArC(CH_3)$(Ph)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=150.2 (s, Ar-C), 148.8 (s, Ar-C), 147.7 (s, Ar-C), 142.9 (s, Ar-C), 128.1 (d, 2C, Ar-CH), 127.0 (d, 2C, Ar-CH), 125.7 (d, Ar-CH), 118.0 (s, Ar-C), 112.2 (d, Ar-CH), 101.5 (d, Ar-CH), 74.5 [s, $ArOC(CH_3)_2$], 56.6 (q, Ar-OCH_3), 55.8 (q, Ar-OCH_3), 50.4 [t, $ArOC(CH_3)_2CH_2$], 39.2 [s, $ArC(CH_3)_2$(Ph)], 32.5 [q, $ArOC(CH_3)_a(CH_3)_b$], 30.1 [q, $ArOC(CH_3)_a(CH_3)_b$], 27.0 [q, $ArC(CH_3)_a$(Ph)] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{25}O_3]^+$=$[M+H]^+$: 313.1798; found: 313.1788.



6,7,8-trimethoxy-2,2,4-trimethyl-4-phenylchromane (**7dm**): General procedure-4 was carried out with alcohol **6dm** (127 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚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 title compound **7dm** (82 mg, 80%) as white solid, recrystallized the solid in dichloromethane/hexane, m. p. 95–96 ˚C. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6dm**)=0.30, R_f(**7dm**)=0.70, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2967, 2925, 2851, 1582, 1491, 1454, 1414, 1257, 1196, 1117, 1079, 1027, 951, 767, 702 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.50–7.00 (m, 5H, Ar-H), 6.43 (s, 1H, Ar-H), 3.92 (s, 3H, Ar-OCH_3), 3.87 (s, 3H, Ar-OCH_3), 3.72 (s, 3H, Ar-OCH_3), 2.34 [d, 1H, J=14.2 Hz, $ArOC(CH_3)_2CH_aCH_b$], 2.04 (d, 1H, J=14.2 Hz, $ArOC(CH_3)_2CH_aCH_b$), 1.67 [s, 3H, $ArOC(CH_3)_a(CH_3)_b$], 1.36 [s, 3H, $ArOC(CH_3)_a(CH_3)_b$], 0.91 [s, 3H, $ArC(Ph)CH_3$] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.9 (s, Ar-C), 146.2 (s, Ar-C), 142.9 (s, Ar-C), 141.9 (s, Ar-C), 141.8 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 126.9 (d, 2C, Ar-CH), 125.7 (d, Ar-CH), 122.8 (s, Ar-CH), 107.1 (d, Ar-CH), 74.6 [s, $ArOC(CH_3)_2$], 61.3 (q, Ar-OCH_3), 61.0 (q, Ar-OCH_3), 56.5 (q, Ar-OCH_3), 50.4 [t, $ArOC(CH_3)_2CH_2$], 39.7 [s, $ArC(Ph)CH_3$], 32.3 [q, $ArOC(CH_3)_a(CH_3)_b$], 29.8 (q, $ArOC(CH_3)_a(CH_3)_b$), 27.1 [q, $ArC(Ph)CH_3$] ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{27}O_4]^+$=$[M+H]^+$: 343.1904; found: 343.1991.

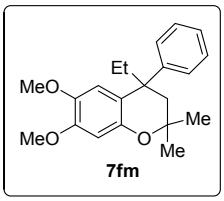


4-(4-chlorophenyl)-6,7-dimethoxy-2,2,4-trimethylchromane (**7em**): General procedure-4 was carried out with alcohol **6em** (128 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **7em** (83 mg, 77%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6em**)=0.40, R_f(**7em**)=0.85, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2968, 2928, 2850, 1506, 1463, 1402, 1254, 1195, 1110, 1009, 913, 828, 729 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.20 (ddd, 2H, J=8.8 and 8.3 Hz, Ar-H), 7.09 (ddd, 2H, J=8.8 and 8.3 Hz, Ar-H), 6.60 (s, 1H, Ar-H), 6.44 (s, 1H, Ar-H), 3.85 (s, 3H, Ar-OCH_3), 3.76 (s, 3H, Ar-OCH_3), 2.27 (d, 1H, J=14.2 Hz, ArOCH_aH_b), 2.04 (d, 1H, J=14.2 Hz, ArOCH$_a$$H_b$),1.65 [s, 3H, ArCOC(C$H_3$)$_a$(CH$_3$)$_b$], 1.33 [s, 3H, ArCOC(CH$_3$)$_a$(C$H_3$)$_b$], 0.89 [s, 3H, ArC(C$H_3$)] ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=149.0 (s, Ar-C), 148.8 (s, Ar-C), 147.6 (s, Ar-C), 143.0 (s, Ar-C), 131.4 (s, Ar-C), 128.4 (d, 2C, Ar-CH), 128.1 (d, 2C, Ar-CH), 117.4 (s, Ar-C), 111.8 (d, Ar-CH), 101.6 (d, Ar-CH), 74.4 [s, ArOC(CH$_3$)$_2$CH$_2$], 56.6 (q, Ar-OCH_3), 55.7 (q, Ar-OCH_3), 50.3 (t, ArOC(CH$_3$)$_2$$CH_2$), 38.9 [s, Ar$C$(Ar)CH$_3$], 32.4 [q, ArOC($CH_3$)$_a$(CH$_3$)$_b$], 29.8 [q, ArOC(CH$_3$)$_a$($CH_3$)$_b$], 27.1 [q, ArC(Ar)$CH_3$] ppm. HR-MS (ESI+) m/z calculated for $[C_{20}H_{24}ClO_3]^+$=$[M+H]^+$: 347.1408; found: 347.1401.



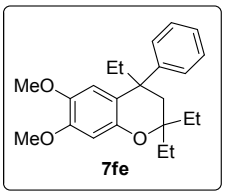
4-(4-chlorophenyl)-2,2-diethyl-6,7-dimethoxy-4-methylchromane (**7ee**): General procedure-4 was carried out with alcohol **6ee** (136 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚C for 24 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 95:5 to 90:10) furnished the title compound **7ee** (86 mg, 75%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6ee**)=0.50, R_f(**7ee**)=0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2965, 2926, 2851, 1507, 1461, 1403, 1260, 1190, 1161, 1109, 1010, 921, 830 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.19 (d, 2H, J=8.8 Ar-H), 7.16 (d, 2H, J=8.8 Hz, Ar-H), 6.58 (s, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 3.86 (s, 3H, Ar-OCH_3), 3.76 (s, 3H, Ar-OCH_3), 2.25 [d, 1H, J=14.2 Hz, ArOC(Et)$_2$CH_aH$_b$], 1.96 [d, 1H, J=14.2 Hz, ArOC(Et)$_2$CH$_a$$H_b$], 1.73–1.60 [m, 1H, ArOC(Et)$_a$(CH_aH$_b$CH$_3$)$_b$], 1.65 [s, 3H, ArOC(CH$_3$)(Ph)],

1.60–1.45 [m, 1H, ArOC(Et)$_a$(CH$_a$*H*$_b$CH$_3$)$_b$], 1.45–1.25 [m, 1H, ArOC(C*H*$_a$H$_b$CH$_3$)$_a$(Et)$_b$], 1.20–1.00 [m, 1H, ArOC(CH$_a$*H*$_b$CH$_3$)$_a$(Et)$_b$], 0.89 [t, 3H, *J*=7.3 Hz, ArOC(CH$_2$C*H*$_3$)$_a$(Et)$_b$], 0.50 [t, 3H, *J*=7.3 Hz, ArOC(Et)$_a$(CH$_2$C*H*$_3$)$_b$] ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=149.1 (s, Ar-C), 148.9 (s, Ar-C), 147.7 (s, Ar-C), 142.9 (s, Ar-C), 131.4 (s, Ar-C), 128.4 (d, 2C, Ar-CH), 128.1 (d, 2C, Ar-CH), 118.1 (s, Ar-C), 111.7 (d, Ar-CH), 101.6 (d, Ar-CH), 79.0 [s, ArO*C*(Et)$_2$], 56.6 (q, Ar-OCH$_3$), 55.8 (q, Ar-OCH$_3$), 45.9 [t, ArOC(Et)$_2$*C*H$_2$], 38.5 [s, Ar*C*(Ar)(CH$_3$)], 32.7 [q, ArC(Ar)(*C*H$_3$)], 30.3 (t, *C*H$_2$CH$_3$), 27.9 (t, *C*H$_2$CH$_3$), 7.6 (q, CH$_2$*C*H$_3$), 7.4 (q, CH$_2$*C*H$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{22}$H$_{28}$ClO$_3$]$^+$=[M+H]$^+$: 375.1721; found: 375.1706.



7fm

4-ethyl-6,7-dimethoxy-2,2-dimethyl-4-phenylchromane (**7fm**): General procedure-4 was carried out with alcohol **6fm** (122 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚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 title compound **7fm** (93 mg, 95%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6fm**)=0.45, R_f(**7fm**)=0.80, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2958, 2919, 2849, 1509, 1462, 1443, 1382, 1247, 1197, 1083, 1018, 999, 802, 703 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.40–7.20 (m, 4H, Ar-H), 7.18–7.10 (m, 1H, Ar-H), 6.68 (s, 1H, Ar-H), 6.45 (s, 1H, Ar-H), 3.86 (s, 3H, Ar-OCH$_3$), 3.80 (s, 3H, Ar-OCH$_3$), 2.24 [d, 1H, *J*=14.2 Hz, ArOC(CH$_3$)C*H*$_a$H$_b$)], 2.14 [d, 1H, *J*=14.2 Hz, ArOC(CH$_3$)CH$_a$*H*$_b$)], 2.12–2.00 (m, 1H, C*H*$_a$H$_b$CH$_3$), 1.98–1.80 (m, 1H, CH$_a$*H*$_b$CH$_3$), 1.34 [s, 3H, ArOC(C*H*$_3$)a(CH$_3$)$_b$], 0.74 [s, 3H, ArOC(CH$_3$)a(C*H*$_3$)$_b$] 0.73 (dd, 3H, *J*=7.3 and 7.3 Hz, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=150.1 (s, Ar-C), 149.1 (s, Ar-C), 148.7 (s, Ar-C), 142.6 (s, Ar-C), 128.0 (d, 2C, Ar-CH), 127.2 (d, 2C, Ar-CH), 125.7 (d, Ar-CH), 114.1 (s, Ar-C), 112.6 (d, Ar-CH), 101.6 (d, Ar-CH), 74.1 [s, Ar(O)*C*(CH$_3$)$_2$], 56.6 (q, Ar-OCH$_3$), 55.7 (q, Ar-OCH$_3$), 44.4 [t, ArOC(CH$_3$)$_2$CH$_2$], 43.1[s, Ar(Ph)*C*CH$_3$CH$_2$], 36.5 (t, *C*H$_2$CH$_3$), 31.2 [q, C(*C*H$_3$)$_a$(CH$_3$)$_b$], 25.6 [q, C(CH$_3$)$_a$(*C*H$_3$)$_b$], 9.4 (q, *C*H$_2$CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{21}$H$_{27}$O$_3$]$^+$=[M+H]$^+$: 327.1955; found: 327.1947.



7fe

2,2,4-triethyl-6,7-dimethoxy-4-phenylchromane (**7fe**): General procedure-4 was carried out with alcohol **6fe** (130 mg, 0.30 mmol), CuI (12 mg, 20 mol %), 2,2'-bipyridine (10 mg, 20 mol %), KO^{t}Bu (101 mg, 0.90 mmol), and DMF (3 mL) at 120 ˚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 title compound **7fe** (96 mg, 90%) as colorless viscous liquid. [TLC control (petroleum ether/ethyl acetate, 80:20), R_f(**6fe**)=0.50, R_f(**7fe**)=0.90, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2964, 2925, 2851, 1619, 1506, 1447, 1250, 1222, 1198, 1160, 1030, 1005, 930, 797, 760, 702 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.30 (d, 2H, J=8.8 Hz, Ar-H), 7.24 (dd, 2H, J=8.3 and 7.3 Hz, Ar-H), 7.14 (t, 1H, J=7.3 Hz, Ar-H), 6.64 (s, 1H, Ar-H), 6.46 (s, 1H, Ar-H), 3.87 (s, 3H, Ar-OCH_3), 3.78 (s, 3H, Ar-OCH_3), 2.15–2.00 [m, 1H, $ArOC(Et)_2CH_aH_b$], 1.95–1.90 (m, 1H, $ArOC(Et)_2CH_aH_b$), 1.70–1.45 [m, 2H, $ArOC(Et)_bCH_2CH_3$], 1.38–1.20 [m, 2H, $ArOC(Et)_aCH_2CH_3$], 1.15–1.00 [m, 1H, $ArC(Ph)CH_aH_bCH_3$], 0.98–0.80 [m, 1H, $ArC(Ph)CH_aH_bCH_3$], 0.91 (t, 3H, J=7.3 Hz, CH_2CH_3), 0.71 (t, 3H, J=7.3 Hz, CH_2CH_3), 0.30 (t, 3H, J=7.3 Hz, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=150.5 (s, Ar-C), 149.2 (s, Ar-C), 148.6 (s, Ar-C), 142.6 (s, Ar-C), 127.9 (d, 2C, Ar-CH), 127.2 (d, 2C, Ar-CH), 125.6 (d, Ar-CH), 114.7 (s, Ar-C), 112.6 (d, Ar-CH), 101.5 (d, Ar-CH), 78.6 [s, $ArOC(Et)_2$], 56.6 (q, Ar-OCH_3), 55.6 (q, Ar-OCH_3), 42.6 [s, $ArC(Ph)(Et)$], 40.5 (t, $ArOC(Et)_2CH_2$), 36.6 (t, CH_2CH_3), 31.5 (t, CH_2CH_3), 26.4 (t, CH_2CH_3), 9.4 (q, CH_2CH_3), 7.3 (q, CH_2CH_3), 7.2 (q, CH_2CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{31}O_3]^+$=$[M+H]^+$: 355.2268; found: 355.2262.