Supporting Information

4*H*-1,2-Benzoxazines with Electron-withdrawing Substituents on the Benzene Ring. Synthesis and Application as Potent Intermediates for Oxygen-Functionalized Aromatic Compounds.

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General Methods

Melting points were determined with a Yazawa micro melting point apparatus and uncorrected. ^{1}H-NMR spectra were recorded on a JEOL GX-Caliber400 using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, and brs = broad singlet. Low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JOEL JMS-O1SG-2 spectrometer.

Cyclization reaction of 2-nitro-3phenylpropane (**1**)

To a suspension of 104.7 mg of *t*-BuONa (97%, 1.05 eq.) in 3 mL of dry THF, was added a solution of 165.4 mg of (**1**) (1.0 mmol) in 5 mL of dry THF. The whole was stirred at r.t. overnight, then the solvent was removed by evaporation. To the residue (the sodium salt of **1**), 7.8 mL of TFA (100 mmol, 100 eq.) was added and the mixture was stirred at r.t. for 1 h. The whole was poured into 50 mL of ice-water, and extracted with $CHCl_3$. The organic phase was washed with saturated NaCl, dried over Na_2SO_4, and the solvent evaporated under reduced pressure to give a residue (203.7

mg), which was column-chromatographed on silica-gel (eluent n-hexane: ethyl acetate=6:1). Removal of the solvent afforded 3-methyl-4*H*-1,2-benzoxazine **2** as colorless amorphous (39.9 mg, 27%). Mp 45.0 – 46.0 °C (recrystallized from ether:n-hexane, colorless plates). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.241-7.171 (m, total 1H), 7.043-6.969 (m, total 3H), 3.296 (s, 2H), 2.100 (s, 3H) Anal. Calcd. for C9H9NO+1/16H_2O: C, 72.89; H, 6.20; N, 9.44. Found: C, 73.05; H, 6.17; N, 9.42. MS *m/z*: 147 (M^+). HRMS Calcd for C_9H_9NO: 147.0684. Found: 147.0646.

Typical Procedure for Synthesis of Methyl 3-aryl-2-nitropropionates 4

To 100 mL of ice-cooled dry THF, was added 9.0 mL of $TiCl_4$ (82.0 mmol, 2.1 eq) in 20 mL of CCl_4. Then, a solution of 4.2265 g of benzaldehyde (39.8 mmol) and 4.8870 g of methylnitroacetate (41.0 mmol, 1.0 eq) in 40 mL of dry THF was added, and the whole was stirred for 2 h at 0 °C. A solution of 16.7555 g of N-methylmorpholine (166 mmol, 4.0 eq.) in 50 mL of dry THF was slowly added over 2 hrs, and the whole was stirred vigorously for 20 h with at 18 °C. Then, 200 mL of water was added, and the whole was extracted with ether. The organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue (7.7677 g). The residue was dissolved in a mixture of 130 mL of $CHCl_3$ and 40 mL of *i*-PrOH. To the solution, 22.0 g of SiO_2 and 6.1002 g of $NaBH_4$ (16.1 mmol) was added, and stirred at r.t. for 4 h. Then, 20 mL of acetic acid was carefully added, and the whole was filtered to remove silica gel. The solvent was evaporated under reduced pressure to give a residue (4.8189 g), which was column-chromatographed on silica gel (eluent n-hexane:AcOEt=7:1-5:1). Removal of the solvent affords **4a** as white solid (2.9195 g, 13.9 mmol, total 35 %). Mp 37.0 - 37.8 °C (recrystallized from n-hexane/$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.342-7.194 (m, total 5H), 5.351 (dd, *J* = 5.68, 9.53 Hz, 1H), 3.830 (s, 3H), 3.567 (dd, *J* = 9.53, 14.4 Hz, 1H), 3.484 (dd, *J* = 5.68, 14.7 Hz, 1H). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70.

Found: C, 57.41; H, 5.33; N, 6.63.

Methyl 3-(4-chlorophenyl)-2-nitropropionate (4b)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.314-7.252 (m, total 2H), 7.161-7.134 (m, total 2H), 5.308 (dd, *J* = 5.68, 9.53 Hz, 1H), 3.835 (s, 3H), 3.536 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.454 (dd, *J* = 5.68, 14.7 Hz, 1H). Anal. Calcd for $C_{10}H_{10}ClNO_4$: C, 49.30; H, 4.14; N, 5.75. Found: C, 49.49; H, 4.29; N, 5.64.

Methyl 3-(4-bromophenyl)-2-nitropropionate (4c)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.447 (d, *J* = 8.43 Hz, 2H), 7.086 (d, *J* = 8.24 Hz, 2H), 5.307 (dd, *J* = 6.23, 12.1 Hz, 1H), 3.835 (s, 3H), 3.521 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.437 (dd, *J* = 5.68, 14.7 Hz, 1H). Anal. Calcd for $C_{10}H_{10}BrNO_4$: C, 41.69; H, 3.50; N, 4.86. Found: C, 41.50; H, 3.69; N, 4.61.

Methyl 3-(3-chlorophenyl)-2-nitropropionate (4d)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.298-7.254 (m, total 2H), 7.216 (s, 1H), 7.101-7.087 (m, total 1H), 5.314 (dd, *J* = 5.68, 9.53 Hz, 1H), 3.858 (s, 3H), 3.519 (dd, *J* = 9.53, 14.8 Hz, 1H), 3.439 (dd, *J* = 5.50, 14.7 Hz, 1H). Anal. Calcd for $C_{10}H_{10}ClNO_4$: C, 49.30; H, 4.14; N, 5.75. Found: C, 49.48; H, 4.29; N, 5.69.

Methyl 3-(3,5-dichlorophenyl)-2-nitropropionate (4e)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.301-7.287 (m, total 1H), 7.113 (d, *J* = 1.83 Hz, 2H), 5.330 (dd, *J* = 5.68, 9.53 Hz, 1H), 3.845 (s, 3H), 3.544 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.461 (dd, *J* = 5.50, 14.7 Hz, 1H). Anal. Calcd for $C_{10}H_9Cl_2NO_4$: C, 43.19; H, 3.26; N, 5.04. Found: C, 43.26; H, 3.39; N, 4.88.

Methyl 3-(4-methoxycarbonylphenyl)-2-nitropropionate (4f)

Mp 90.0 – 91.0 °C (recrystallized from n-hexane/$CHCl_3$, colorless cubes). ^{1}H-NMR (400

MHz, $CDCl_3$) δ (ppm) :7.993 (d, J = 8.06 Hz, 2H), 7.289 (d, *J* = 8.06 Hz, 2H), 5.363 (dd, *J* = 5.68, 9.34 Hz, 1H), 3.909 (s, 3H), 3,624 (s, 3H), 3.624 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.537 (dd, *J* = 5.86, 14.5 Hz, 1H). Anal. Calcd for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90; N, 5.24. Found: C, 53.77; H, 4.97; N, 5.09.

Methyl 3-(4-diisopropylcarbamoylphenyl)-2-nitropropionate (4g)

Mp 117.5 – 119.0 °C (recrystallized from n-hexane/$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.292-7.212 (m, total 5H), 5.353 (dd, *J* = 5.68, 9.53 Hz, 1H), 3.842 (s, 3H), 3.586 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.493 (dd, *J* = 5.68, 14.7 Hz, 1H), 1.617-1.163 (m, total 14H). Anal. Calcd for $C_{17}H_{24}N_2O_5$: C, 60.70; H, 7.19; N, 8.33. Found: C, 60.66; H, 7.13; N, 8.27.

Methyl 3-(4-trifluoromethylphenyl)-2-nitropropionate (4h)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.590 (d, *J* = 8.06 Hz, 2H), 7.344 (d, *J* = 8.06 Hz, 2H), 5.362 (dd, *J* = 5.68, 9.71 Hz, 1H), 3.851 (s, 3H), 3.633 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.548 (dd, *J* = 5.68, 14.8 Hz, 1H). Anal. Calcd for $C_{11}H_{10}F_3NO_4$: C, 47.66; H, 3.64; N, 5.05. Found: C, 47.54; H, 3.71; N, 4.90.

Methyl 3-(4-cyanophenyl)-2-nitropropionate (4i)

Mp 56.0 – 57.0 °C (recrystallized from n-hexane/$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.641-7.620 (m, total 2H), 7.355-7.260 (m, total 2H), 5.349 (dd, *J* = 5.50, 9.53 Hz, 1H), 3.853 (s, 3H), 3.631 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.548 (dd, *J* = 5.68, 14.8 Hz, 1H). Anal. Calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.61; H, 4.48; N, 11.94.

Methyl 3-(4-nitrophenyl)-2-nitropropionate (4j)

Mp 62.0 – 63.1 °C (recrystallized from ether, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :8.214-8.180 (m, total 2H), 7.422-7.394 (m, total 2H), 5.381 (dd, *J* = 5.50, 9.53 Hz, 1H), 3.862 (s, 3H), 3.684 (dd, *J* = 5.50, 14.7 Hz, 1H), 3.598 (dd, *J* = 5.50, 14.7 Hz, 1H). Anal. Calcd for

$C_{10}H_{10}N_2O_6$: C, 47.25; H, 3.97; N, 11.02. Found: C, 47.28; H, 4.16; N, 11.12.

Methyl 3-(4-methylphenyl)-2-nitropropionate (4k)

Mp 32.1 – 32.7 °C recrystallized from n-hexane/$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.130-7.071 (m, total 4H), 5.320 (dd, *J* = 5.86, 9.53 Hz, 1H), 3.828 (s, 3H), 3.522 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.441 (dd, *J* = 5.68, 14.5 Hz, 1H), 2.317 (s, 3H). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.14; H, 5.83; N, 6.17.

Methyl 3-(4-methoxyphenyl)-2-nitropropionate (4l)

Mp 49.0 – 50.0 °C (recrystallized from ether, colorless cubes). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.135-7.107 (m, total 2H), 6.857-6.823 (m, total 2H), 5.297 (dd, *J* = 5.86, 9.53 Hz, 1H), 3.824 (s, 3H), 3.781 (s, 3H), 3.502 (dd, *J* = 9.53, 14.7 Hz, 1H), 3.422 (dd, *J* = 5.86, 14.7 Hz, 1H). Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48; N, 5.86. Found: C, 55.35; H, 5.55; N, 5.79.

Typical Procedure for Cyclization Reaction of Methyl 3-aryl-2-nitropropionates

3-Methoxycarbonyl-4*H*-1,2-benzoxazine (5a)

To ice-cooled 0.45 mL of TFSA (5.0 mmol, 10 eq.), a solution of 106.3 mg of methyl 2-nitro-3-phenylpropionate **4a** (0.5 mmol) in 10 mL of dry $CHCl_3$ was slowly added. The mixture was stirred at 50 °C for 30 min, then the whole was poured into 50 mL of ice-water, and extracted with $CHCl_3$. The organic phase was washed with brine, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue (98.0 mg), which was column-chromatographed on silica-gel (eluent n-hexane:ethyl acetate=5:1). Removal of the solvent afforded 3-methoxycarbonyl-4*H*-1,2-benzoxazine **5a** as white powder (84.5mg, 85%).

Mp 64.0-65.0 °C (recrystallized from ether, colorless plates). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.267-7.224 (m, 1H), 7.119-7.038 (m, total 3H), 3.940 (s, 3H), 3.659 (s, 2H). Anal. Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.74; N, 7.33. Found: C, 62.74; H, 4.86; N, 7.32.

7-Chloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5b)

Mp 96.0 - 97.0 °C (recrystallized from ether, colorless plates). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.099-7.032 (m, total 3H), 3.944 (s, 3H), 3.625 (s, 2H). Anal. Calcd for $C_{10}H_8ClNO_3$: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.17; H, 3.78; N, 6.06.

7-Bromo-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5c)

Mp 110.0 - 111.0 °C (recrystallized from ether, colorless cubes). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.238-7.218 (m, total 2H), 7.204 (d, 1H, *J* = 1.83 Hz), 3.924 (s, 3H), 3.589 (s, 2H). Anal. Calcd for $C_{10}H_8BrNO_3$: C, 44.47; H, 2.99; N, 5.19. Found: C, 44.36; H, 3.03; N, 5.17.

6-Chloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5d)

Mp 111.0 - 112.0 °C (recrystallized from ether, colorless cubes). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.208 (dd, 1H, *J* = 2.38, 8.61 Hz), 7.105 (d, 1H, *J* = 2.56 Hz), 6.998 (d, 1H, *J* = 8.79 Hz), 3.943 (s, 3H), 3.636 (s, 2H). Anal. Calcd for $C_{10}H_8ClNO_3$: C, 53.23; H, 3.57; N, 6.21. Found: C, 53.20; H, 3.71; N, 6.22.

8-Chloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5d')

Mp 89.0 - 90.0 °C (recrystallized from n-hexane: ethyl acetate, yellow powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.309-7.285 (m, 1H), 7.037-7.020 (m, total 2H), 3.947 (s, 3H), 3.675 (s, 2H). Anal. Calcd for $C_{10}H_8ClNO_3$: C, 53.23; H, 3.57; N, 6.21. Found: 53.36; H, 3.78; N, 6.04.

6,8-Dichloro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5e)

Mp 83.0 – 84.0 °C (recrystallized from ether, colorless needle). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.311 (d, *J* = 2.38 Hz, 1H), 7.301-7.023 (m, total 1H), 3.951 (s, 3H), 3.654 (s, 2H). Anal. Calcd for $C_{10}H_7Cl_2NO_3$: C, 46.07; H, 2.71; N, 5.39. Found: C, 46.11; H, 2.89; N, 5.39.

3,7-Dimethoxycarbonyl-4*H*-1,2-benzoxazine (5f)

Dec. 144.0 - 146.0 °C (recrystallized from n-hexane/$CHCl_3$, colorless needles). ^{1}H-NMR (400

MHz, $CDCl_3$) δ (ppm) : 7.782 (dd, *J* = 1.65, 7.88 Hz, 1H), 7.719 (d, *J* = 1.65 Hz, 1H), 7.255-7.183 (m, total 1H), 3.950 (s, 3H), 3.922 (s, 3H), 3.705 (s, 2H). Anal. Calcd for $C_{12}H_{11}NO_5$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.74; H, 4.53; N, 5.52.

7-Diisopropylcarbamoyl-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5g)

Dec. 123.0 – 124.0 °C (recrystallized from ether, colorless plates). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.134 (d, *J* = 7.69 Hz, 1H), 7.049 (dd, *J* = 1.47, 7.88 Hz, 1H), 6.998 (d, *J* = 1.10 Hz, 1H), 3.944 (s, 3H), 3.665 (s, 2H), 1.589-1.191 (m, total 14H). Anal. Calcd for $C_{17}H_{22}N2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.12; H, 6.80; N, 8.63.

7-Trifluoromethyl-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5h)

Mp 98.0 – 99.0 °C (recrystallized from ether, colorless plates). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.344-7.212 (m, total 3H), 3.926 (s, 3H), 3.682 (s, 2H). Anal. Calcd for $C_{11}H_8F_3NO_3$: C, 50.97; H, 3.11; N, 5.40. Found: C, 50.95; H, 3.27; N, 5.30.

7-Cyano-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5i)

Dec. 140.0 - 143.0 °C (recrystallized from n-hexane/$CHCl_3$, colorless needles). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.409-7.362 (m, total 2H), 7.260-7.234 (m, total 1H), 3.958 (s, 3H), 3.712 (s, 2H). Anal. Calcd for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.73; N, 12.96. Found: C, 60.92; H, 3.90; N, 12.76.

7-Nitro-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5j)

Dec. 145.0 – 146.0 °C (recrystallized from n-hexane/$CHCl_3$, colorless needles). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.989 (dd, *J* = 2.20, 8.24 Hz, 1H), 7.938 (d, *J* = 2.38 Hz, 1H), 7.315 (d, *J* = 8.43 Hz, 1H), 3.968 (s, 3H), 3.762 (s, 2H). Anal. Calcd for $C_{10}H_8N_2O_5$+1/8H_2O: C, 50.37; H, 3.49; N, 11.75. Found: C, 50.27; H, 3.43; N, 11.74.

7-Methyl-3-methoxycarbonyl-4*H*-1,2-benzoxazine (5k)

Mp 94.5 – 95.0 °C (recrystallized from n-hexane/$CHCl_3$, white powder). ^{1}H-NMR (400 MHz,

$CDCl_3$) δ (ppm) : 7.259 (d, *J* = 2.02 Hz, 1H), 6.990-6.869 (m, total 2H), 3.931 (s, 3H), 3.613 (s, 2H). Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.23; H, 5.46; N, 6.61.

7-Methoxy-3-methoxycarbonyl-4H-1,2-benzoxazine (5l)

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 6.996 (d, *J* = 8.24 Hz, 1H), 6.674 (dd, *J* = 2.56, 8.43 Hz, 1H), 6.598 (d, *J* = 2.57 Hz, 1H), 3.934 (s, 3H), 3.792 (s, 3H), 3.596 (s, 2H).

8-Oxo-1-oxa-2-aza-spiro[4,5]deca-2,6,9-triene-3-carboxylic acid methyl ester (6)

Mp 94.5 – 96.0 °C (recrystallized from n-hexane/$CHCl_3$, colorless needles). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 6.832 (d, *J* = 10.1 Hz, 2H), 6.271 (d, *J* = 10.1 Hz, 2H), 3.906 (s, 3H), 3.345 (s, 2H). Anal. Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.71; H, 4.47; N, 6.76. MS *m/z*: 207 (M^+). HRMS Calcd for $C_{10}H_9NO_4$: 207.0532. Found: 207.0497.

Typical Procedure for the Diels-Alder Reaction of o-Benzoquinone-methide Generated from 3-Methoxycarbonyl-4*H*-1,2-benzoxazines

2-Phenylchroman (8a)

A solution of 124.4 mg of **5a** (0.65 mmol) and 1.3648 g of styrene (13.1 mmol, 20 eq.) in 15 mL of dry toluene was heated at 90 °C with stirring for 12 h. Then the solvent was evaporated under reduced pressure to give a residue, which was column-chromatographed on silica-gel (eluent n-hexane:ethyl acetate = 30:1). Removal of the solvent afforded 2-phenylchroman **8a** as white solid (76.8 mg, 56%). Mp 39.0 – 39.5 °C (recrystallized from n-hexane, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.437-7.291 (m, total 5H), 7.139-7.075 (m, total 2H), 6.917-6.850 (m, total 2H), 5.063 (dd, *J* = 2.57, 10.3 Hz, 1H), 3.040-2.955 (m, total 1H), 2.827-2.765 (m, total 1H), 2.246-2.040 (m, total 2H). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71; N, 0.00. Found: C, 85.44; H, 6.82; N, 0.00. MS *m/z*: 210 (M^+). HRMS Calcd for $C_{15}H_{14}O$: 210.1045. Found: 210.1043.

7-Chloro-2-phenylchroman (8b)

Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.323-7.175 (m, total 5H), 6.919 (d, *J* = 8.06 Hz, 1H), 6.848 (d, *J* = 2.02 Hz, 1H), 6.769 (dd, *J* = 6.05, 8.06 Hz, 1H), 4.991 (dd, *J* = 2.57, 10.1 Hz, 1H), 2.889-2.816 (m, total 1H), 2.712-2.649 (m, total 1H), 2.178-2.113 (m, total1H), 2.044-1.943 (m, total 1H). MS *m/z*: 244 (M^+). HRMS Calcd for $C_{15}H_{13}ClO$: 244.0655. Found: 244.0615.

7-Methoxycarbonyl-2-phenylchroman (8f)

Mp 86.0 – 87.0 °C (recrystallized from ether, white cubes). ^{1}H-NMR (400 MHz, $CDCl_3$) _ (ppm) : 7.591 (d, *J* = 1.65 Hz, 1H), 7.589-7.527 (m, total 1H), 7.431-7.303 (m, total 5H), 7.138 (d, *J* = 7.88 Hz, 1H), 5.106 (dd, *J* = 2.56, 10.1 Hz, 1H), 3.888 (s, 3H), 3.063-2.977 (m, total 1H), 2.872-2.807 (m, total 1H), 2.285-2.221 (m, total 1H) 2.148-2.047 (m, total 1H). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; N, 0.00. Found: C, 75.93; H, 5.99; N, 0.00.

7-Diisopropylcarbamoyl-2-phenylchroman (8g)

Mp 138.0 – 139.0 °C (recrystallized from ether, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.427-7.264 (m, total 5H), 7.077 (d, *J* = 7.69 Hz, 1H), 6.844-6.801 (m, total 2H), 5.083 (dd, *J* = 2.38, 9.89 Hz, 1H), 3.025-2.940 (m, total 1H), 2.824-2.761 (m, total 1H), 2.263-2.198 (m, total 1H), 2.135-2.034 (m, total 1H), 1.600-1.191 (m, total 14H). Anal. Calcd. for $C_{22}H_{27}NO_2$: C, 78.30; H, 8.06; N, 4.15. Found: C, 78.19; H,8.10; N, 4.12.

7-Cyano-2-phenylchroman (8i)

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) :7.424-7.321 (m, total 5H), 7.177-7.126 (m, total 3H, m), 5.104 (dd, *J* = 2.38, 10.1 Hz, 1H), 3.064-2.979 (m, total 1H), 2.879-2.815 (m, total 1H), 2.295-2.231 (m, total 1H), 2.153-2.044 (m, total 1H). MS *m/z*: 235 (M^+). HRMS Calcd for $C_{16}H_{13}NO$: 235.0997. Found: 235.1039.

Hydrolysis of 3-Methoxycarbonyl-4*H*-1,2-benzoxazines. Typical Procedure.

2-Hydroxyphenylacetonitrile (10a)

To a solution of 251.9 mg of **5a** in 10 mL of dry THF was added 10 mL of 2 N aqueous NaOH. The mixture was stirred at r.t. for 1h, then the whole was acidified with 12 N HCl, extracted with ethyl acetate. The organic phase was washed with saturated NaCl, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue (168.2 mg), which was column-chromatographed on silica-gel (eluent n-hexane:ethyl acetate=1:1, 5% of acetic acid added). Removal of the solvent afforded 2-hydroxyphenylacetnitrile **10a** as white powder (140.1 mg, 80%). Mp 118.5 – 119.0 °C (recrystallized from n-hexane:$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) : 7.354 (d, *J* = 7.70 Hz, 1H), 7.215 (dt, *J* = 1.38, 7.70 Hz, 1H), 6.967 (dt, *J* = 1.10, 7.70 Hz, 1H), 6.781 (d, *J* = 7.97 Hz, 1H), 5.086 (brs, 1H), 3.728 (s, 2H). Anal. Calcd for C_8H_7NO: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.07; H, 5.45; N, 10.45.

MS *m/z*: 133 (M^+). HRMS Calcd for C_8H_7NO: 133.0501. Found: 133.0526.

4-Chloro-2-hydroxyphenylacetonitrile (10b)

Mp 116.0 – 117.0 °C (recrystallized from ether, colorless needles). ^{1}H-NMR (400 MHz, acetone-d_6) δ (ppm) : 9.364 (s, 1H), 7.337 (d, *J* = 8.24 Hz, 1H), 6.962-6.911 (m, total 2H), 3.781 (s, 2H). Anal. Calcd for C_8H_6ClNO: C, 57.33; H, 3.61; N, 8.36. Found: C, 57.52; H, 3.85; N, 8.39.

4-Cyano-2-hydroxyphenylacetonitrile (10i)

Dec 174.0 – 175.0 °C (recrystallized from n-hexane:$CHCl_3$, white powder). ^{1}H-NMR (400 MHz, acetone-d_6) δ (ppm) : 9.643 (s, 1H), 7.434 (d, *J* = 7.88 Hz, 1H), 7.187 (dd, *J* = 1.47, 7.88 Hz, 1H), 7.122 (d, *J* = 1.47 Hz, 1H), 3.791 (s, 2H). Anal. Calcd for $C_9H_6N_2O\_1/12H_2O$: C, 67.70; H, 3.89; N, 17.55. Found: C, 67.79; H, 4.16; N, 17.25. MS *m/z*: 158 (M^+). HRMS Calcd for $C_9H_6N_2O$: 158.0480. Found: 158.0508.