Coumarin-4-ylmethoxycarbonyls as Phototriggers for Alcohols and Phenols

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Synthesis

1,2,3,4-Di-*O*-isopropylidene-D-galactopyranosyl 7-methoxycoumarin-4-ylmethoxycarbonate (1a).

To a stirred solution of 82.9 mg (0.318 mmol) of 1,2,3,4-di-*O*-isopropylidene-D-galactopyranose in CH_2Cl_2 (2 mL) and CH_3CN (2.5 mL) was added 49.3 mg (0.404 mmol) of 4-dimethylaminopyridine and 104.0 mg (0.387 mmol) of 7-methoxycoumarin-4-ylmethoxycarbonyl chloride. The reaction mixture was stirred at room temperature for 45 min. The solvents were removed with rotovap. Purification by flash column chromatography (15 g of SiO_2, CH_2Cl_2/CH_3OH = 25/1) gave 123.9 mg (0.237 mmol. 94% yield) of **1a.**

1a. ^{1}H NMR ($CDCl_3$) δ 1.34 (3H, s), 1.35 (3H, s), 1.46 (3H, s), 1.52 (3H, s), 3.88 (3H, s), 4.09 (1H, ddd, J=1.6, 5.5 & 8.0 Hz), 4.26 (1H, dd, J= 1.6 & 7.8 Hz), 4.31-4.43 (3H, m), 4.64 (1H, dd, J=2.4 & 7.8 Hz), 5.27 (1H, d, J=14 Hz), 5.34 (1H, d, J=14 Hz), 5.55 (1H, d, J=4.9 Hz), 6.39 (1H, s), 6.85 (1H, s), 6.87 (1H, d, J= 8.4 Hz), 7.41 (1H, d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$/TMS) δ 24.49, 24.91, 25.95, 26.03, 55.80, 64.53, 65.67, 67.32, 70.37, 70.68, 70.82, 96.25, 101.23, 108.88, 109.79, 110.33, 110.44, 112.67, 124.43, 148.37, 154.48, 155.58, 160.71, 162.90; UV $\lambda_{max}/nm\ (\varepsilon)$ solvent A: 322 (12,100), solvent C: 323 (13,100).

1,2,3,4-Di-*O*-isopropylidene-D-galactopyranosyl 6-bromo-7-hydroxycoumarin-4-ylmethoxycarbonate (1b).

To a stirred solution of 325.8 mg (1.202 mmol) of 6-bromo-7-hydroxy-4-hydroxymethylcoumarin (**2b**) in CH_3CN (5 mL) was added 353.2 mg (2.89 mmol) of 4-dimethylaminopyridine and 264.0 mg (1.31 mmol) of 4-nitrophenyl chloroformate. The reaction mixture was stirred for 6 hr at room temperature. Then, another 152.5 mg (1.25 mmol) of 4-dimethylaminopyridine and 515 mg (1.99 mmol) of 1,2,3,4-di-*O*-isopropylidene-D-galactopyranose were added to the reaction mixture. After 24 hr, the mixture was diluted with $CHCl_3$, washed with 0.5 M citric acid and sat. NaCl, and dried over $MgSO_4$. Purification by column chromatography (50 g of SiO_2, n-Hexane/EtOAc = 3/2) gave 221.9 mg (0.398 mmol. 33% yield) of **1b**.

1b. ^{1}H NMR ($CDCl_3$/TMS) δ 1.34 (3H, s), 1.35 (3H, s), 1.47 (3H, s), 1.53 (3H, s), 4.08-4.13 (2H, m), 4.25 (1H, dd, J=1.5, 7.8 Hz), 4.33-4.37 (3H, m), 4.63 (1H, dd, J=2.3, 7.8 Hz), 5.24 (1H, d, J=14 Hz), 5.27 (1H, d, J=14 Hz), 5.55 (1H, d, J=5 Hz), 6.41 (1H, s), 7.04 (1H, s), 7.62 (1H, s); ^{13}C NMR ($CDCl_3$/TMS) δ 24.45, 24.86, 25.90, 25.99, 64.19, 65.67, 67.43, 70.32, 70.64, 70.78, 96.21, 104.37, 106.86, 108.91, 109.80, 111.24, 111.72, 126.84, 147.57, 154.36, 154.41, 155.83, 160.29; UV $\lambda_{max}/nm\ (\varepsilon)$ solvent A: 374 (15,000), solvent B: 376 (14,000).

1,2,3,4-Di-*O*-isopropylidene-D-galactopyranosyl 7-diethylaminocoumarin-4-ylmethoxycarbonate (1c).

To a stirred suspension of 271.6 mg (1.04 mmol) of 7-diethylamino-4-hydroxymethylcoumarin in CH_2Cl_2 (7 mL) was added 141.7 mg (1.16 mmol) of 4-dimethylaminopyridine and232.0 mg (1.15 mmol) of 4-nitrophenyl chloroformate. The reaction mixture was stirred for 10 hr at room temperature. Thin layer chromatography indicated that the formation of intermediate 4-nitrophenyl carbonate completed. Then, another 142.2 mg (1.16 mmol) of 4-dimethylaminopyridine and 265.9 mg (1.02 mmol) of 1,2,3,4-di-*O*-isopropylidene-D-galactopyranose were added to the reaction mixture. After 20 hr, the mixture was diluted with CH_2Cl_2, washed with sat. $NaHCO_3$ and sat. NaCl, and dried over $MgSO_4$. Purification by flash column chromatography (23 g of SiO_2, CH_2Cl_2/CH_3OH = 85/1 then CH_2Cl_2/CH_3OH = 50/1) gave 440.9 mg (0.826 mmol. 81% yield) of **1c**.

1c. ^{1}H NMR ($CDCl_3$/TMS) δ 1.21(6H, t, J=7.3 Hz), 1.34 (3H, s), 1.35 (3H, s), 1.46 (3H, s), 1.52 (3H, s), 3.41 (4H, q, J=7.3 Hz), 4.08 (1H, ddd, J=1.5, 5 & 8.5 Hz), 4.27 (1H, dd, J=1.5, 7.8 Hz), 4.33-4.37 (3H, m), 4.63 (1H, dd, J=2.3, 7.8 Hz), 5.23 (1H, d, J=14 Hz), 5.30 (1H, d, J=14 Hz), 5.55 (1H, d, J=4.9 Hz), 6.17 (1H, s), 6.50 (1H, d, J=2.4 Hz), 6.57 (1H, dd, J=2.4, 8.9 Hz), 7.28 (1H, d, J=8.9 Hz); ^{13}C NMR ($CDCl_3$/TMS) δ 12.42(x 2), 24.49, 24.92, 25.95, 26.04, 44.77(x 2), 64.73, 65.65, 67.13, 70.39, 70.66, 70.81, 96.24, 97.87, 105.86, 106.78, 108.69, 108.88, 109.74, 124.40, 148.60, 150.64, 154.58, 156.28, 161.71; UV $\lambda_{max}/nm\ (\varepsilon)$ solvent B:

250 (11,400), 396 (17,300).

1,2,3,4-Di-*O*-isopropylidene-D-galactopyranosyl 6,7-dimethoxycoumarin-4-ylmethoxycarbonate (1d).

To a stirred solution of 65.4 mg (0.251 mmol) of 1,2,3,4-di-*O*-isopropylidene-D-galactopyranose in CH_2Cl_2 (5 mL) and CH_3CN (2 mL) was added 39.0 (0.32 mmol) of 4-dimethylaminopyridine and 90.8 mg (0.304 mmol) of 6,7-dimethoxycoumarin-4-ylmethoxycarbonylchloride. The reaction mixture was stirred at room temperature for 2 hr. The solvent was removed with rotovap. Purification by flash column chromatography (20 g of SiO_2, CH_2Cl_2/CH_3OH = 80/1 then CH_2Cl_2/CH_3OH = 50/1) gave 123.9 mg (0.237 mmol. 94% yield) of **1d.**

1d. ^{1}H NMR ($CDCl_3$) δ 1.34 (3H, s), 1.35 (3H, s), 1.46 (3H, s), 1.52 (3H, s), 3.93 (3H, s), 3.95 (3H, s), 4.09 (1H, ddd, J=1.5, 5.5 & 8.0 Hz), 4.26 (1H, dd, J=1.5 & 7.8 Hz), 4.31-4.44 (3H, m), 4.64 (1H, dd, J= 2.4 & 7.8 Hz), 5.28 (1H, d, J=15 Hz), 5.34 (1H, d, J=15 Hz), 5.54 (1H, d, J= 4.9 Hz), 6.43 (1H, s), 6.84 (1H, s), 6.87 (1H, s); ^{13}C NMR ($CDCl_3$/TMS) δ 24.48, 24.90, 25.94, 26.02, 56.38, 56.53, 64.67, 65.68, 67.36, 70.36, 70.67, 70.82, 96.24, 100.35, 103.91, 108.88, 109.36, 109.79, 110.80, 146.41, 148.12, 149.77, 153.01, 154.52, 160.89; UV $\lambda_{max}/nm\ (\varepsilon)$ solvent A: 290 (4,500), 344 (10,800).

1,2,3,4-Di-*O*-isopropylidene-D-galactopyranosyl 6-nitroveratryloxycarbonate (1e).

To a stirred solution of 143.8 mg (0.552 mmol) of 1,2,3,4-di-*O*-isopropylidene-D-galactopyranose in CH_2Cl_2 (3.5 mL) and CH_3CN (1 mL) was added 84.3 mg (0.69 mmol) of 4-dimethylaminopyridine and 180.5 mg (0.655 mmol) of 6-nitroveratryloxycarbonyl chloride. The reaction mixture was stirred at room temperature for 3 hr. The solvents were removed with rotovap. Purification by flash column chromatography (20 g of SiO_2, CH_2Cl_2/CH_3OH = 98/1 then CH_2Cl_2/CH_3OH = 25/1) gave 169.1 mg (0.339 mmol. 61% yield) of **1e.**

1e. ^{1}H NMR ($CDCl_3$) δ 1.32 (3H, s), 1.34 (3H, s), 1.46 (6H, s), 3.96 (3H, s), 4.01 (3H, s), 4.11 (1H, ddd, J= 1.0, 5.5 & 7.0 Hz), 4.26 (1H, dd, J=1.0 & 8.0 Hz), 4.32-4.37 (3H, m), 4.62 (1H, dd, J=2.2 & 8.0 Hz), 5.53 (1H, d, J=4.9 Hz), 5.59 (1H, d, J=14 Hz), 5.63 (1H, d, J=14 Hz), 7.09 (1H, s), 7.74 (1H, s); ^{13}C NMR ($CDCl_3$/TMS) δ 24.47, 24.91, 25.92 (X 2), 56.40, 56.58, 65.71, 66.30, 67.10, 70.35, 70.67, 70.88, 96.25, 108.09, 108.82, 109.47, 109.75, 127.12, 139.41, 148.16, 153.81, 154.67; UV $\lambda_{max}/nm\ (\varepsilon)$

solvent A: 344 (5,400).

Phenyl 6-Bromo-7-hydroxycoumarin-4-ylmethoxycarbonate (3).

To a stirred suspension of 134.9 mg (0.498 mmol) of **2b** in CH_3CN (3.5 mL) was added 147 μL (0.84 mmol) of diisopropyl ethylamine and 63 μL (0.50 mmol) of phenyl chloroformate. The reaction mixture was stirred at room temperature for 3.5 hr. The solvents were removed with rotovap. Purification by flash column chromatography (17g of SiO_2, n-Hexane/EtOAc = 5/2) gave 117.7mg (0.301 mmol. 60% yield) of **3.**

3. ^{1}H NMR ($CDCl_3$/TMS) δ 5.37 (2H, s), 6.49 (1H, s), 7.05 (1H, s), 7.10-7.15 (3H, m), 7.40-7.45 (2H, m), 7.67 (1H, s); ^{13}C NMR ($CDCl_3$/TMS) δ 65.28, 103.20, 106.32, 109.90, 110.35, 121.22, 126.40, 128.74, 129.69, 148.60, 150369, 152.43, 153.89, 157.59, 159.52; UV $\lambda_{max}/nm\ (\varepsilon)$ solvent A: 372 (17,900).

6-Bromo-7-methoxymethoxy-4-hydroxymethylcoumarin (4).

To a stirred suspension of 1.0846 g (4.001 mmol) of **2b** in CH_2Cl_2 (10 mL) was added 836 μL (4.80 mmol) of diisopropyl ethylamine and 365 μL (4.81 mmol) of chloromethyl methyl ether. The reaction mixture was stirred at room temperature for 40 min. The reaction mixture was diluted with $CHCl_3$, washed with 0.5 M citric acid and dried over $MgSO_4$. The solvents were removed with rotovap and high vacuum rotovap to give 1.065 g (3.380 mmol, 85% yield) of **4**.

4. ^{1}H NMR ($CDCl_3$/TMS) δ 7.70 (s, 1H), 7.16 (s, 1H), 5.32 (s, 2H), 3.52 (s, 3H), 6.52 (t, 1H, J = 1.3 Hz), 4.86 (dd, 2H, J = 5.6, 1.3 Hz), 2.07 (t, 1H, J = 5.6 Hz); ^{13}C NMR (DMSO-d_6/TMS) δ 56.23 (q), 59.06 (t), 94.80 (t), 103.51 (d), 107.49 (s), 108.96 (d), 112.75 (s), 128.19 (d), 153.51 (s), 155.13 (s), 155.76 (s), 159.93 (s); IR (ATR) 3508, 1703, 1604, 1267, 1158, 1095, 1083, 1032, 1009, 974, 894, 842 cm^{-1}.

6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl chloride (5).

In a glass pressure bottle (Hyperglasstor, THG-A2, TAIATSU Techno) 1.9834 g (6.684 mmol) of triphogene was placed. To this

195.4 μL (0.483 mmol) of aliquat^R 336 in n-hexane (4 mL) was added. The mixture was stirrer at room temperature for 19 hr to generate phosgene. To a stirred solution of 321.7 mg (1.021 mmol) of 4 in toluene (2 mL) and THF (3 mL) was added the phosgene solution (4 mL). The reaction mixture was stirred at 0°C for 3.5 hr. The solvents were removed under reduced pressure. The residual solid was washed with $CHCl_3$ and n-hexane (1/1 v/v) twice to give 352.0 mg (0.932 mmol, 91% yield) of **5**.

5. ^{1}H NMR ($CDCl_3$/TMS) δ 3.53 (3H, s, MOM), 5.33 (2H, s, MOM), 5.42 (2H, d, J=1.5, H-4), 6.43 (1H, s, H-3), 7.19 (1H, s, H-8), 7.64 (1H, s, H-5); ^{13}C NMR ($CDCl_3$/TMS) δ 56.73(q), 67.08(t), 95.17(t), 104.19(d), 108.82(s), 111.77(d), 112.58(s), 127.27(s), 145.28(s), 150.62(s), 154.27(s), 156.74(s), 159.49(s); IR (ATR) 1756, 1719, 1603, 1273, 1164, 1151 cm^{-1}.

3-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-1,2-dioctanoyl glycerol.

To a stirred solution of 169.1 mg (0.491 mmol) of 1,2-dioctanoyl glycerol (diC_8) in CH_3CN (4 mL) were added 115.3 mg (0.944 mmol) of 4-dimethylaminopyridine and 192.3 mg (0.509 mmol) of **5**. The reaction mixture was stirred at room temperature for 40 min. The solvents were removed with rotovap. Purification by flash column chromatography (35 g of SiO_2, n-hexane/AcOEt = 35/10) gave 321.1 mg (0.468 mmol. 95% yield) of the title compound.

^{1}H NMR ($CDCl_3$) δ 7.68 (s, 1H), 7.17 (s, 1H), 6.42 (t, 1H, J = 1.0 Hz), 5.32 (s, 1H), 5.30 (m, 1H), 5.28 (d, 1H, J = 1.0 Hz), 4.45 (dd, 1H, J = 11.9, 4.0 Hz), 4.35 (dd, 1H, J = 11.5, 4.6 Hz), 4.30 (dd, 1H, J = 11.5, 5.6 Hz), 4.19 (dd, 1H, J = 11.9, 5.6 Hz), 3.52 (s, 3H), 2.35 (t, 2H, J = 7.6 Hz), 2.33 (t, 2H, J = 7.6 Hz), 1.62 (4H, m), 1.28 (16H, m), 0.87 (6H, m); ^{13}C NMR ($CDCl_3$/TMS) δ 173.2 (s), 172.9 (s), 159.8 (s), 156.5 (s), 154.2 (s), 147.0 (s), 127.4 (d), 112.1 (s), 111.8 (d), 108.6 (s), 104.1 (d), 95.1 (t), 68.4 (s), 66.6 (t), 64.4 (t), 61.6 (t), 56.7 (q), 34.1 (t), 34.0 (t), 31.6 (t), 29.0 (t), 28.9 (t), 24.8 (t), 22.5 (t), 14.0 (q); IR (ATR) 1735, 1606, 1441, 1277, 1202, 1160 cm$^{-1;}$ MS (ESI) m/z 707.10 ($C_{32}H_{45}{}^{79}BrO_{11}+Na^+$), 709.90 ($C_{32}H_{45}{}^{81}BrO_{11}+Na^+$) .

3-(6-Bromo-7-hydroxy-4-ylmethoxycarbonyl)-1,2-dioctanoyl glycerol (7).

A solution of 79.9 mg (0.117 mmol) of 3-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-1,2-dioctanoyl glycerol in trifluoroacetic acid (2 mL) was stirred at room temperature for 15 min. The solvent was evaporated by rotovap and high vacuum rotovap to give 71.9 mg (0.112 mmol. 96% yield) of **7**.

7. ^{1}H NMR ($CDCl_3$) δ 7.63 (s, 1H), 7.05 (s, 1H), 6.40 (t, 1H, J = 1.3 Hz), 5.33 (m, 1H), 5.28 (d, 2H, J = 1.3 Hz), 4.45 (dd, 1H, J = 11.9, 4.0 Hz), 4.35 (dd, 1H, J = 11.5, 4.3 Hz), 4.31 (dd, 1H, J = 11.5, 5.3 Hz), 4.20 (dd, 1H, J = 11.9, 5.6 Hz), 2.35 (t, 2H, J = 7.6 Hz), 2.34 (t, 2H, J = 7.6 Hz), 1.62 (m, 4H), 1.28 (m, 16H), 0.87 (m, 6H); ^{13}C NMR ($CDCl_3$/TMS) δ 173.4 (s), 173.0 (s), 160.2 (s), 155.9 (s), 154.4 (s), 154.2 (s), 147.4 (s), 126.8 (d), 111.6 (s), 111.3 (d), 106.9 (s), 104.4 (d), 68.5 (s), 66.6 (t), 64.4 (t), 61.7 (t), 34.1 (t), 34.0 (t), 31.6 (t), 29.0 (t), 28.9 (t), 24.8 (t), 22.6 (t), 14.0 (q); IR (ATR) 3375 (broad), 1724, 1607, 1441, 1409, 1280, 1218, 1160 cm$^{-1;}$ MS (ESI) m/z 663.00 ($C_{30}H_{41}{}^{79}BrO_{10}+Na^+$), 664.80 ($C_{30}H_{41}{}^{81}BrO_{10}+Na^+$).

O-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-*N*-*tert*-butoxycarbonyl-L-tyrosine methyl ester.

To a stirred solution of 236.8 mg (0.802 mmol) of *N*-*tert*-butoxycarbonyl-L-tyrosine methyl ester in CH_3CN (6 mL) were added 184.4 mg (1.51 mmol) of 4-dimethylaminopyridine and 268.8 mg (0.71 mmol) of **5**. The reaction mixture was stirred at room temperature for 15 min. The solvents were removed with rotovap. Purification by flash column chromatography (30 g of SiO_2, CH_2Cl_2/CH_3OH = 100/1 then CH_2Cl_2/CH_3OH = 80/1) gave 455.1 mg (0.71 mmol. 100% yield) of the title compound.

^{1}H NMR ($CDCl_3$) δ 7.72 (s, 1H), 7.20 7.12 (m, 5H), 6.47 (s, 1H), 5.38 (s, 2H), 5.32 (s, 2H), 5.17 (d, 1H, J = 7.9 Hz), 4.59 (m, 1H), 3.72 (s, 3H), 3.52 (s, 3H), 3.15 (dd, 1H, J = 13.9, 5.6 Hz), 3.04 (dd, 1H, J = 13.9, 6.3 Hz), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$/TMS) δ 171.9 (s), 159.6 (s), 156.2 (s), 154.8 (s), 154.0 (s), 152.7 (s), 149.6 (s), 146.9 (s), 134.3 (s), 130.3 (d), 127.3 (d), 120.6 (d), 111.9 (s), 111.6 (d), 108.4 (s), 103.8 (d), 94.9 (t), 79.7 (s), 64.5 (t), 56.5 (q), 54.1 (d), 52.1 (q), 37.4 (t), 28.0 (q); IR (ATR) 1735, 1605, 1507, 1366, 1243, 1218, 1156 cm$^{-1;}$ MS (ESI) m/z 657.95 ($C_{28}H_{30}{}^{79}BrNO_{11}+Na^+$), 659.75 ($C_{28}H_{30}{}^{81}BrNO_{11}+Na^+$) .

O-(6-Bromo-7-hydroxycoumarin-4-ylmethoxycarbonyl)-L-tyrosine methyl ester hydrochloride (8).

Hydrogen chloride gas was introduced into a stirred solution of 62.6 mg (0.098 mmol) of *O*-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-*N*-*tert*-butoxycarbonyl-L-tyrosine methyl ester in CH_2Cl_2 (4 mL) at room tremperature for 2 min. The reaction mixture was stirred at room temperature for 3 hr. The solvent and the excess HCl were removed by rotovap and high vacuum rotovap to give 52.0 mg (0.098 mmol 100% yield) of **8**.

8 (HCl salt). ^{1}H NMR ($CDCl_3$) δ 7.83 (s, 1H), 7.36-7.25 (m, 4H), 6.84 (s, 1H), 6.32 (s, 1H), 5.47 (s, 2H), 4.36 (dd, 1H, J = 7.3, 6.3 Hz), 3.82 (s, 3H), 3.31 (dd, 1H, J = 14.2, 6.3 Hz), 3.20 (dd, 1H, J = 14.2, 7.3 Hz); ^{13}C NMR ($CDCl_3$/TMS) δ 170.3 (s), 162.3 (s), 159.3 (s), 155.7 (s), 154.5 (s), 152.2 (s), 150.3 (s), 133.7 (s), 131.8 (d), 129.5 (d), 122.8 (d), 112.0 (s), 110.8 (d), 108.1 (s), 104.4 (d), 66.4 (t), 55.1 (q), 53.7 (d), 36.7 (t); IR (ATR) 3383, 1175, 1736, 1608, 14006, 1272, 1249, 1235 cm$^{-1;}$ MS (ESI) m/z 491.90 ($C_{21}H_{18}{}^{79}BrNO_8+H^+$), 493.75 ($C_{21}H_{18}{}^{81}BrNO_8+H^+$).

5’-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-2’,3’-O-isopropylideneadenosine.

To a stirred suspension of 248.4 mg (0.757 mmol) of **4** in CH_3CN (6 mL) were added 194.8 mg (1.60 mmol) of 4-dimethylaminopyridine and 167.5 mg (0.814 mmol) of 4-nitrophenyl chloroformate at room temperature. After 1.5 hr, another 110.3 mg (0.903 mmol) of 4-dimethylaminopyridine and 253.9 mg (0.826 mmol) of 2’,3’-isopropylideneadenosine were added. The reaction mixture was stirred at room temperature for 3.5 hr. The solvents were removed with rotovap. The residue was diluted with $CHCl_3$ (30 mL), and washed with 0.5 M citric acid and sat. NaCl. The organic layer was dried over $MgSO_4$, and the solvent was removed by rotovap and high vacuum rotovap. Purification by flash column chromatography (35 g of SiO_2, CH_2Cl_2/CH_3OH = 30/1 then CH_2Cl_2/CH_3OH = 21/1) gave 307.4 mg (0.474 mmol. 63% yield) of the product.

^{1}H NMR ($CDCl_3$/TMS) δ 1.42 (s, 3H), 1.63 (s, 3H), 3.51 (s, 3H), 4.41 (dd, 1H, J = 11.2, 5.9 Hz), 4.51 (dd, 1H, J = 11.2, 4.0 Hz), 4.56 (m, 1H), 5.16 (dd, 1H, J = 6.3, 3.0 Hz), 5.22 (d, 2H, J = 1.7 Hz), 5.31 (s, 2H), 5.51 (dd, 1H, J = 6.3, 2.0 Hz), 6.19 (d, 1H, J = 2.0 Hz), 6.31 (br, 2H), 6.44 (t, 1H, J = 1.7 Hz), 7.12 (s, 1H), 7.60 (s, 1H), 7.94 (s, 1H), 8.32 (s, 1H); ^{13}C NMR ($CDCl_3$/TMS) δ 25.3 (q), 27.0 (q), 56.6 (q), 64.2 (t), 68.1 (t), 81.4 (d), 84.3 (d), 84.8 (d), 90.7 (d), 95.0 (t), 103.9 (d), 108.5 (s), 111.5 (d), 112.0 (s), 114.5 (s), 120.0 (s), 127.2 (d), 139.5 (d), 147.0 (s), 149.1 (s), 153.1 (d), 153.9 (s), 154.0 (s), 155.8 (s), 156.3 (s),159.9 (s); IR (ATR) 1731, 1637, 1604, 1266, 1214, 1155 cm^{-1}; MS (ESI) m/z 647.95 ($C_{26}H_{26}{}^{79}BrN_5O_{10}+H^+$), 649.75 ($C_{26}H_{26}{}^{81}BrN_5O_{10}+H^+$).

5’-(6-Bromo-7-hydroxy-4-ylmethoxycarbonyl)adenosine (9).

To a stirred solution of 181.9 mg (0.281 mmol) of 5’-(6-Bromo-7-methoxymethoxycoumarin-4-ylmethoxycarbonyl)-2’,3’-O-isopropylideneadenosine in trifluoroacetic acid (2 mL) was added 80 μL of water at room temperature. After 20 hr, the solvents were evaporated by rotovap and high vacuum rotovap. Purification by flash column chromatography (15 g of SiO_2,

CH_2Cl_2/CH_3OH = 15/1 then CH_3OH) gave 92.5 mg (0.117 mmol. 42% yield) of **9**·2TFA.

9·(2TFA salt). ^{1}H NMR ($CDCl_3$/TMS) δ 8.31 (s, 1H), 8.15 (s, 1H), 7.84 (s, 1H), 7.29 (s, 2H), 6.81 (s, 1H), 6.14 (s, 1H), 5.93 (d, 1H, J = 4.9 Hz), 5.60 (d, 1H, J = 5.6 Hz), 5.44 (d, 1H, J = 5.3 Hz), 5.38 (s, 2H), 4.67 (m, 1H), 4.47 (dd, 1H, J = 11.2, 3.6 Hz), 4.38 (dd, 1H, J = 11.2, 6.2 Hz), 4.26 (m, 1H), 4.14 (m, 1H); ^{13}C NMR ($CDCl_3$/TMS) δ 159.8 (s), 156.1 (s), 154.2 (s), 153.9 (s), 152.7 (d), 152.4 (s), 149.4 (s), 149.2 (s), 139.7 (d), 128.2 (d), 119.2 (s), 109.3 (s), 108.3 (d), 107.3 (s), 103.4 (d), 87.8 (d), 81.3 (d), 72.9 (d), 70.3 (d), 68.2 (t), 64.6 (t); IR (ATR) 3337 (broad), 3184 (broad), 1685, 1646, 1604, 1406, 1271, 1249, 1206, 1139 cm^{-1}; MS (ESI) m/z 563.90 ($C_{21}H_{18}{}^{79}BrN_5O_9+H^+$), 565.75 ($C_{21}H_{18}{}^{81}BrN_5O_9+H^+$).

Quantum efficiency measurement.

Into a pyrex test tube of 12 mm diameter was placed 2 mL of 10 μM substrate solution in K-MOPS solution (pH 7.2) containing 1% DMSO. The solution was irradiated at 350 nm using either two or four RPR 350 nm lamps. Aliquots of 10 μL were removed periodically and analyzed by HPLC. The light output for the quantum efficiencies measurement was performed using ferrioxalate actinometry.

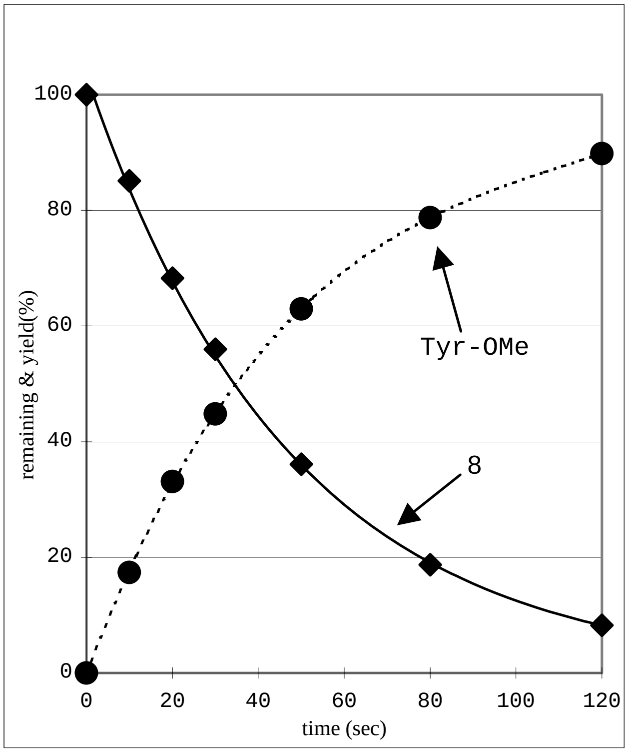

Figure 1. Time course of photolysis of Bhcmoc-Tyr-OMe (8) in solvent A upon 350 nm irradiation (two RPR 350 nm lamps). Concentrations of 8 and Tyr-OMe were quantified by HPLC analysis.

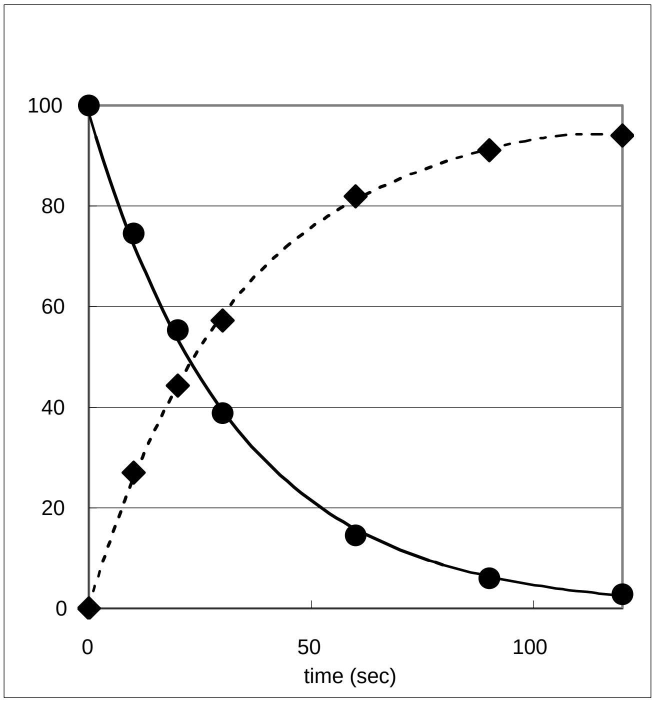

Figure 2. Time course of photolysis of 5’-Bhcmoc-adenosine (9) in solvent A upon 350 nm irradiation (four RPR 350 nm lamps). Concentrations of 9 and adenosine were quantified by HPLC analysis.

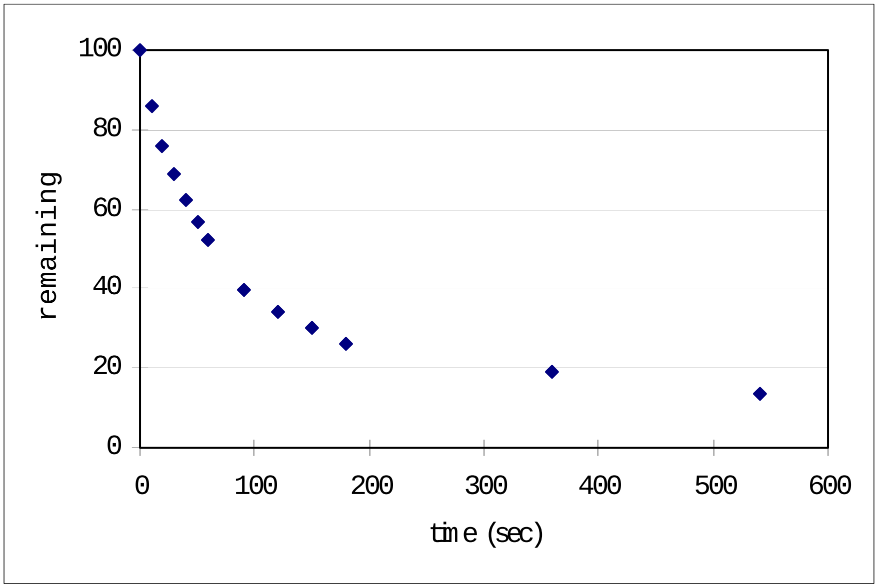

Figure 3. Time course of photolysis of Bhcmoc-dic8 (7) in solvent A upon 350 nm irradiation (two RPR 350 nm lamps). Concentrations of 7 were quantified by HPLC analysis.