The Dearomative Annulation between N-2-Pyridylamidine and CO\textsubscript{2} toward Pyrido[1,2-\textit{a}]-1,3,5-triazin-4-ones

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1. General Considerations

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc) and used without further purification. \(^1\)H NMR and \(^{13}\)C NMR spectra were recorded at ambient temperature on a 300, 400 or 500 MHz NMR spectrometer (75, 100 or 125 MHz for \(^{13}\)C). NMR experiments are reported in \(\delta\) units, parts per million (ppm), and were referenced to CDCl\(_3\) (\(\delta 7.26\) or 77.0 ppm) or DMSO-d\(_6\) (\(\delta 2.50\) or 39.52 ppm) as the internal standard. The coupling constants \(J\) are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). All melting points were uncorrected.

2. General Procedure for the Preparation of \(N\)-Substituted Amidines 1

To a stirred solution of substituted 2-aminopyridine (10 mmol) in DMF (5.0 mL) was added NaH (60% dispersion in mineral oil, 12 mmol) at 0 °C, and the mixture was stirred at the same temperature for 30 min. Substituted benzonitrile (12 mmol) was then added to the reaction mixture and the mixture stirred at room temperature until TLC indicated the total consumption of the substituted 2-aminopyridine. The reaction was quenched by the addition of 5% aqueous NaHCO\(_3\) (10 mL) and the mixture extracted with EtOAc. The extract was washed with brine and dried over Na\(_2\)SO\(_4\). The solvent was then evaporated, and the residue was purified by column chromatography using a mixture of petroleum ether and EtOAc as the eluent to afford the desired \(N\)-substituted amidine 1.

3. Experimental Procedures

In a glovebox, a 20 mL Schlenk tube equipped with a stir bar was charged with 1 (0.1 mmol), base (0.3 mmol, 3 eq.) and toluene (2 mL). The tube was sealed with a Teflon lined cap. The tube was then evacuated and back-filled with carbon dioxide for 3 times. The reaction mixture was stirred at 120 °C for 24 h in oil bath. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product.
4. The Synthesis of 3^2

Procedures a: mixture of 2-deoxythymidine (10.0 g, 41.3 mmol) and imidazole (11.8 g, 173 mmol) in anhydrous DMF was stirred at room temperature for 5 min. Then tert-butyldimethylsilyl chloride (13.1 g, 86.7 mmol) was added, and the mixture was stirred for another 12 h. After adding water (100 mL), the reaction mixture was extracted with hexane, dried with Na_2SO_4 and concentrated under vacuum to give 3a as a white solid. Mp = 141-143 °C.

Procedures b: A mixture of 3a (3.00 g, 6.40 mmol) and ammonium sulfate (337 mg, 2.55 mmol) was dissolved in hexamethyldisilazane (11.7 g, 72.5 mmol) in a dry flask, and the resulting mixture was heated at reflux for 4 h. After the solvents were removed under vacuum, the residue was dissolved in CH_2Cl_2. The solution was washed with saturated NaHCO_3 solution, water, and brine, dried with Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography (hexane/Et_2O, 19:1) to give 3 as a yellow oil.

5. The Procedures of 2p toward Artificial Nucleosides
Under N₂, a 20 mL Schlenk tube equipped with a stir bar was charged with 2p (0.1 mmol), 3 (0.12 mmol, 1.2 eq.), triethylamine (0.3 mmol, 3 eq.), Pd(OAc)₂ (0.01 mmol, 0.1 eq.), dry acetonitrile (2 mL). The mixture was heated at 60 °C for 20 h. The reaction was concentrated under vacuum, and the crude product was purified by silica gel column chromatography (hexane/EtOAc, 3:1 + 0.1% of Et₃N) to give 4a and 4b.
6. Characterization Data for the Products

2-Phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2a):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2a (18.9 mg, 85% yield) as white solid. Mp. 190-191 °C.

1H NMR (CDCl3, 400 MHz): δ 9.07 (d, J = 6.9 Hz, 1H), 8.57 (d, J = 7.9 Hz, 2H), 8.01 (t, J = 7.8 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.55 (t, J = 8.8 Hz, 1H), 7.50-7.46 (m, 2H), 7.31 (t, J = 6.9 Hz, 1H); 13C NMR (CDCl3, 100 MHz): δ 169.6, 155.5, 151.3, 141.5, 135.8, 132.6, 129.9, 129.5, 128.4, 125.5, 117.7.

2-(p-Tolyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2b):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2b (19.2 mg, 81% yield) as white solid. Mp. 228-229 °C.

1H NMR (CDCl3, 400 MHz): δ 9.05 (d, J = 6.9 Hz, 1H), 8.46 (d, J = 7.9 Hz, 2H), 7.99 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.30-7.26 (m, 3H), 2.43 (s, 3H); 13C NMR (CDCl3, 100 MHz): δ 169.6, 155.5, 151.3, 143.4, 141.3, 133.1, 129.9, 129.6, 129.2, 125.4, 117.4, 21.7; HRMS (ESI) m/z calcd for C14H12N3O+(M + H)+ 238.0975, found 238.0976.

2-(o-Tolyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2c):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2c (20.0 mg, 84% yield) as white solid. Mp. 164-166 °C.

1H NMR (CDCl3, 400 MHz): δ 9.09 (d, J = 6.8 Hz, 1H), 8.05-8.01 (m, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.39-7.34 (m, 2H), 7.30-7.26 (m, 2H), 2.68 (s, 3H); 13C NMR (CDCl3, 100 MHz): δ 173.1, 155.1, 150.1, 141.6, 138.5, 136.3, 131.5, 130.7, 129.7, 128.5, 125.3, 117.9, 21.6; HRMS (ESI) m/z calcd for C14H12N3O+(M + H)+ 238.0975, found 238.0980.

2-(Naphthalen-1-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2d):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2d (19.7 mg, 72% yield) as white solid. Mp. 171-173 °C.

1H NMR (CDCl3, 400 MHz): δ 9.07 (d, J = 6.8 Hz, 1H), 8.98 (d, J = 8.5 Hz, 1H), 8.32 (d, J = 7.2 Hz, 1H), 7.99-7.96 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.58-7.54 (m, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 6.9 Hz, 1H); 13C NMR (CDCl3, 100 MHz): δ 172.4, 155.0, 150.7, 141.7, 133.9, 133.9, 132.1, 130.9, 130.4, 129.6, 128.5, 127.1, 126.0, 125.9, 125.3, 124.9, 118.1 HRMS (ESI) m/z calcd for C17H13N3O+(M + H)+ 274.0975, found 274.0977.

2-(4-Chlorophenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2e):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et₃N) give 2e (21.3 mg, 83% yield) as white solid. Mp. > 250 °C.

¹H NMR (CDCl₃, 300 MHz) δ 9.11-9.08 (m, 1H), 8.56-8.51 (m, 1H), 8.08-8.02 (m, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.37-7.32 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.6, 155.5, 151.2, 141.7, 139.1, 134.3, 130.9, 130.0, 128.7, 125.5, 117.8; HRMS (ESI) m/z calcd for C₁₃H₉ClN₃O⁺ (M + H)⁺ 258.0429, found 258.0432.

2-(4-Bromophenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2f):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et₃N) give 2f (26.0 mg, 86% yield) as white solid. Mp. > 250 °C.

¹H NMR (CDCl₃, 400 MHz) δ 9.09 (d, J = 6.7 Hz, 1H), 8.45 (d, J = 8.1 Hz, 2H), 8.05 (t, J = 7.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 6.7 Hz, 1H);

¹³C NMR (CDCl₃, 100 MHz) δ 168.7, 155.5, 151.2, 141.7, 134.8, 131.7, 131.1, 130.0, 127.8, 125.5, 117.9; HRMS (ESI) m/z calcd for C₁₃H₉BrN₃O⁺ (M + H)⁺ 301.9924, found 301.9924.

2-(4-Fluorophenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2g):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et₃N) give 2g (16.9 mg, 70% yield) as white solid. Mp. 232-234 °C.

¹H NMR (DMSO-d₆, 400 MHz): δ 9.03 (d, J = 6.7 Hz, 1H), 8.55-8.51 (m, 2H), 8.32 (t, J = 7.8 Hz, 1H), 7.81 (d, J = 8.7 Hz), 7.60 (t, J = 6.8 Hz), 7.41 (t, J = 8.7 Hz);

¹³C NMR (DMSO-d₆, 75 MHz): δ 167.5, 165.8 (d, J = 21.8 Hz); HRMS (ESI) m/z calcd for C₁₃H₉FN₃O⁺ (M + H)⁺ 242.0724, found 242.0726.

2-(4-(Trifluoromethyl)phenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2h):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et₃N) give 2h (21.8 mg, 75% yield) as white solid. Mp. 169-172 °C.

¹H NMR (CDCl₃, 400 MHz) δ 9.08 (d, J = 6.8 Hz, 1H), 8.66 (d, J = 8.1 Hz, 2H), 8.07 (t, J = 7.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 3H), 7.38 (t, J = 6.9 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.1, 155.5, 151.1, 142.0, 139.1, 133.7 (q, J = 32.0 Hz), 130.0, 129.7, 125.6, 125.2 (q, J = 4.0 Hz), 123.9 (q, J = 271.0 Hz), 118.3; HRMS (ESI) m/z calcd for C₁₄H₉F₃N₃O⁺ (M + H)⁺ 292.0692, found 292.0692.

2-(Furan-2-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2i):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et$_3$N) give 2i (15.1 mg, 71% yield) as white solid. Mp. 209-210 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 9.02 (d, $J$ = 6.9 Hz, 1H), 8.01 (t, $J$ = 7.8 Hz, 1H), 7.68 (br, 2H), 7.54 (d, $J$ = 3.0 Hz, 1H), 7.30 (t, $J$ = 6.8 Hz, 1H), 6.57 (br, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 161.3, 155.7, 150.50, 150.47, 147.0, 142.0, 130.1, 125.1, 118.2, 117.7, 112.8; HRMS (ESI) m/z calcd for C$_{11}$H$_8$N$_3$O$_2$ (M + H)$^+$ 214.0611, found 214.0613.

2-(Thiophen-2-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2j):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et$_3$N) give 2j (17.6 mg, 77% yield) as white solid. Mp. 192-193 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 9.02 (d, $J$ = 6.8 Hz, 1H), 8.18 (d, $J$ = 3.7 Hz, 1H), 7.98 (t, $J$ = 7.8 Hz, 1H), 7.62-7.60 (m, 2H), 7.27 (t, $J$ = 6.9 Hz, 1H), 7.16 (t, $J$ = 4.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 165.6, 155.5, 150.7, 141.63, 141.58, 133.3, 132.6, 130.0, 128.6, 125.0, 117.3; HRMS (ESI) m/z calcd for C$_{11}$H$_8$N$_3$O$_2$ (M + H)$^+$ 230.0383, found 230.0385.

7-Methyl-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2k):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et$_3$N) give 2k (19.4 mg, 82% yield) as white solid. Mp. 200-201 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.88 (s, 1H), 8.54 (d, $J$ = 7.9 Hz, 2H), 7.85 (d, $J$ = 7.9 Hz, 1H), 7.54 (t, $J$ = 7.0 Hz, 1H), 7.49-7.45 (m, 2H), 2.45 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.9, 154.1, 151.3, 144.1, 135.9, 132.4, 129.4, 128.40, 128.35, 127.6, 124.9, 18.3; HRMS (ESI) m/z calcd for C$_{14}$H$_{12}$N$_3$O (M + H)$^+$ 238.0975, found 238.0980.

7-Chloro-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2l):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et$_3$N) give 2l (18.0 mg, 70% yield) as yellow solid. Mp. 232-234 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 9.09 (s, 1H), 8.56 (d, $J$ = 7.9 Hz, 2H), 7.94 (d, $J$ = 9.2 Hz, 1H), 7.60 (d, $J$ = 8.9 Hz, 1H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.50 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 169.7, 154.1, 150.3, 142.5, 135.4, 133.0, 129.6, 128.5, 127.8, 126.5, 125.8; HRMS (ESI) m/z calcd for C$_{13}$H$_{10}$ClN$_3$O (M + H)$^+$ 258.0429, found 258.0436.

7-Bromo-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2m):

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et$_3$N) give 2m (17.8 mg, 59% yield) as yellow solid. Mp. 242-244 °C.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.20 (s, 1H), 8.56 (d, $J$ = 7.7 Hz, 2H), 7.94 (d, $J$ = 9.2 Hz, 1H), 7.65 (d, $J$ = 9.3 Hz, 1H), 7.58 (t, $J$ = 7.2 Hz, 1H), 7.50 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 169.7, 154.1, 150.3, 142.5, 135.4, 133.0, 129.6, 128.5, 127.8, 126.5, 125.8; HRMS (ESI) m/z calcd for C$_{13}$H$_{10}$ClN$_3$O (M + H)$^+$ 258.0429, found 258.0436.
Hz, 2H), 8.04 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 9.2 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H); 
13C NMR (CDCl3, 100 MHz) δ 169.7, 154.2, 150.2, 144.7, 135.4, 133.0, 130.1, 129.6, 128.5, 126.5, 112.3; HRMS (ESI) m/z calcd for C13H9BrN3O+ (M + H)+ 301.9924, found 301.9921.

2,7-Diphenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2n):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et3N) give 2n (13.7 mg, 46% yield) as yellow solid. Mp. 245-247 °C.

1H NMR (CDCl3, 300 MHz) δ 9.30 (d, J = 2.2 Hz, 1H), 8.62-8.58 (m, 2H), 8.30 (dd, J = 9.1 Hz, 1H), 7.78 (d, J = 9.1 Hz, 1H), 7.68-7.64 (m, 2H), 7.57-7.46 (m, 6H); 
13C NMR (CDCl3, 100 MHz) δ 169.2, 154.3, 151.4, 141.1, 135.8, 134.5, 132.6, 131.9, 129.53, 129.50, 129.4, 128.4, 126.84, 126.78, 125.5; HRMS (ESI) m/z calcd for C19H14N3O+ (M + H)+ 300.1131, found 300.1133.

9-Methyl-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2o):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2o (20.9 mg, 88% yield) as white solid. Mp. 171-174 °C.

1H NMR (CDCl3, 400 MHz) δ 8.94 (d, J = 6.8 Hz, 1H), 8.59 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 6.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.49-7.45 (m, 2H), 7.19 (t, J = 6.8 Hz, 1H), 2.66 (s, 3H); 
13C NMR (CDCl3, 100 MHz) δ 168.4, 154.8, 151.9, 140.1, 136.0, 134.7, 132.5, 129.5, 128.3, 127.6, 117.0, 17.4; HRMS (ESI) m/z calcd for C14H12N3O+ (M + H)+ 238.0975, found 238.0982.

9-Iodo-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2p):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2p (20.2 mg, 58% yield) as white solid. Mp. 214-215 °C.

1H NMR (CDCl3, 400 MHz): δ 9.04 (d, J = 6.6 Hz, 1H), 8.64 (d, J = 7.4 Hz, 2H), 8.53 (d, J = 7.2 Hz, 1H), 7.59-7.52 (m, 1H), 7.52-7.48 (m, 2H), 7.03 (t, J = 6.8 Hz, 1H); 
13C NMR (CDCl3, 100 MHz): δ 169.9, 153.9, 151.7, 151.2, 135.5, 133.1, 130.3, 128.5, 118.1, 96.7; HRMS (ESI) m/z calcd for C13H9IN3O+ (M + H)+ 349.9785, found 349.9783.

2-Phenyl-8-(trifluoromethyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2q):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et3N) give 2q (18.3 mg, 63% yield) as white solid. Mp. 181-183 °C.

1H NMR (CDCl3, 400 MHz) δ 9.10 (d, J = 7.2 Hz, 1H), 8.53 (d, J = 7.9 Hz, 2H), 7.88 (s, 1H), 7.57 (t, J = 7.0 Hz, 1H), 7.49-7.46 (m, 2H), 7.36 (d, J = 7.2 Hz, 1H); 
13C NMR (CDCl3, 100 MHz) δ 170.3, 155.4, 150.4, 142.2 (q, JCF = 36.0 Hz), 135.0, 133.2, 131.6, 129.7, 128.5,
123.3 (q, $J_{C-F} = 5.0$ Hz), 121.3 (q, $J_{C-F} = 273.0$ Hz), 112.5 (q, $J_{C-F} = 3.0$ Hz); HRMS (ESI) m/z calcd for C$_{14}$H$_{9}$F$_{3}$N$_{3}$O$^+$ (M + H)$^+$ 292.0692, found 292.0699.

8-Methoxy-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2r):
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et$_3$N) give 2r (17.7 mg, 70% yield) as white solid. Mp. 221-223 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.87 (d, $J = 7.1$ Hz, 1H), 8.49 (d, $J = 7.8$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.47-7.43 (m, 2H), 6.85-6.83 (br, 2H), 4.00 (s, 3H);

$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 169.4, 169.0, 157.4, 151.4, 153.9, 132.3, 131.1, 129.3, 128.3, 111.6, 101.7, 56.9; HRMS (ESI) m/z calcd for C$_{14}$H$_{12}$N$_{3}$O$_2$+ (M + H)$^+$ 254.0924, found 254.0934.

9-((2R,5R)-4-((tert-butyldimethylsilyl)oxy)-5-((tert-butyldimethylsilyl)oxy)methyl)-2,5-dihydrofuran-2-yl)-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (4a):
Flash column chromatography on a silica gel (ethyl acetate: hexane, 1: 3 + 0.1% of Et$_3$N) give 4a (16.0 mg, 31% yield) as white solid. Mp. 158-160 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 9.00 (d, $J = 6.7$ Hz, 1H), 8.61 (t, $J = 8.0$ Hz, 3H), 7.57 (t, $J = 7.0$ Hz, 1H), 7.51-7.48 (m, 2H), 7.29 (t, $J = 7.0$ Hz, 1H), 5.95-5.92 (m, 1H), 4.21 (t, $J = 2.3$ Hz, 1H), 4.08-4.00 (m, 2H), 3.45-3.40 (m, 1H), 2.33-2.27 (m, 1H), 0.83 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.2, 152.7, 151.6, 150.5, 139.1, 138.9, 136.1, 132.5, 129.5, 128.4, 128.0, 117.6, 100.7, 79.4, 63.1, 25.9, 25.6, 18.5, 18.1, -4.9, -5.1, -5.3, -5.4; HRMS (ESI) m/z calcd for C$_{30}$H$_{44}$N$_{3}$O$_{4}$Si$_{2}$+ (M + H)$^+$ 566.2865, found 566.2905.

9-((2R,5R)-4-((tert-butyldimethylsilyl)oxy)-5-((tert-butyldimethylsilyl)oxy)methyl)-4-oxotetrahydrofuran-2-yl)-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (4b):
Flash column chromatography on a silica gel (ethyl acetate: hexane, 1: 3 + 0.1% of Et$_3$N) give 4b (12.7 mg, 28% yield) as yellow oil.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 9.05 (dd, $J = 1.3$, 6.9 Hz, 1H), 8.53-8.51 (m, 3H), 7.59-7.56 (m, 1H), 7.51-7.48 (m, 2H), 7.37 (t, $J = 7.1$ Hz, 1H), 5.95-5.92 (m, 1H), 4.21 (t, $J = 2.3$ Hz, 1H), 4.08-4.00 (m, 2H), 3.45-3.40 (m, 1H), 2.33-2.27 (m, 1H), 0.83 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 213.1, 168.7, 152.8, 151.2, 137.6, 137.3, 132.9, 132.5, 129.5, 128.7, 128.5, 117.2, 82.4, 72.4, 62.6, 44.9, 25.7, 18.2, -5.5, -5.7; HRMS (ESI) m/z calcd for C$_{24}$H$_{30}$N$_{3}$O$_{4}$Si$^+$ (M + H)$^+$ 452.2007, found 452.2000.
7. References
8. Copies of the $^1$H NMR and $^{13}$C NMR Spectra

2-phenyl-4$H$-pyrido[1,2-$a$][1,3,5]triazin-4-one (2a)
2-(p-tolyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2b)
2-(o-toly)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2c)
2-(naphthalen-1-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2d)
2-(4-chlorophenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2e)

\[ \text{Structure Image} \]

\[ \text{S15} \]
2-(4-bromophenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2f)
2-(4-fluorophenyl)-4H-pyrido[1,2-α][1,3,5]triazin-4-one (2g)
2-(4-(trifluoromethyl)phenyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2h)
2-(furan-2-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2i)
2-(thiophen-2-yl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2j)
7-methyl-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2k)
7-chloro-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2l):
7-bromo-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2m)
2,7-diphenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2n)
7-methyl-2-phenyl-4H-pyrido[1,2-\textit{a}]1,3,5\textit{triazin}-4-one (2o)
9-iodo-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2p)
2-phenyl-8-(trifluoromethyl)-4H-pyrido[1,2-a][1,3,5]triazin-4-one (2q)
8-methoxy-2-phenyl-4H-pyrido[1,2-\textit{a}]1,3,5\textit{triazin}-4-one (2r)
9-((2R,5R)-4-((tert-butyl(dimethyl)silyl)oxy)-5-((tert-butyl(dimethyl)silyl)oxy)methyl)-2,5-dihydrofuran-2-yl)-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazine-4-one (4a)
9-((2R,5R)-5-(((tert-butyldimethylsilyl)oxy)methyl)-4-oxotetrahydrofuran-2-yl)-2-phenyl-4H-pyrido[1,2-a][1,3,5]triazin-4-one (4b)