Supplementary Information

The Dearomative Annulation between *N*-2-Pyridylamidine and CO_2 toward Pyrido[1,2-*a*]-1,3,5-triazin-4-ones

Minfang Xia, Weiming Hu, Song Sun, Jin-Tao Yu, Jiang Cheng *

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, and Institute for Natural and Synthetic Organic Chemistry, Changzhou University, Changzhou 213164, P. R. China.

Email: jiangcheng@cczu.edu.cn

Table of Contents

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 δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) or DMSO-d_6 (δ 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.

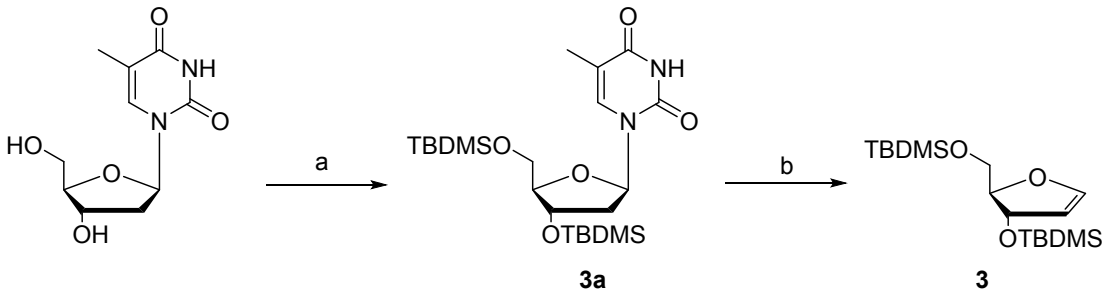
2. General Procedure for the Preparation of *N*-Substituted Amidines 1[1]

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_2SO_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.

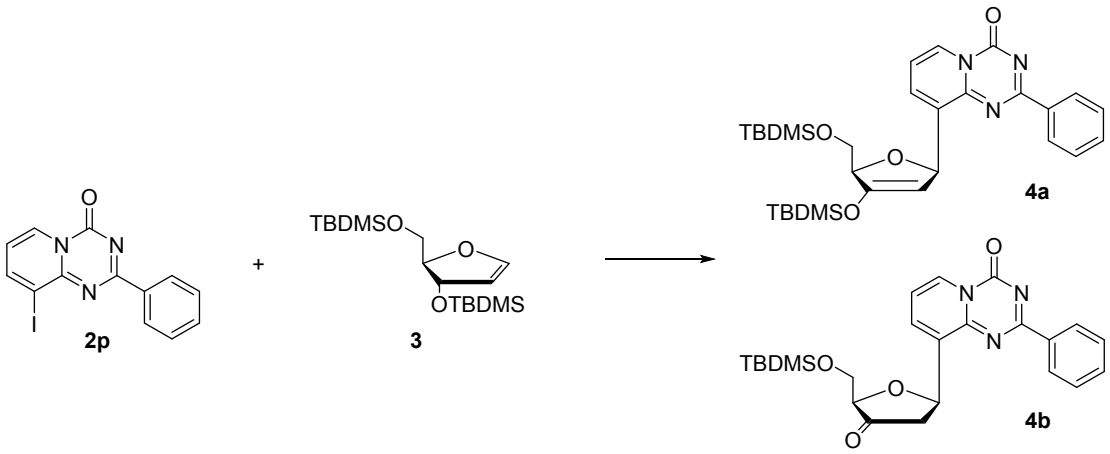
4. The Synthesis of 3[2]



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 ^oC.

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.

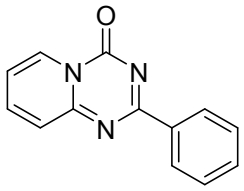
5.The Procedures of 2p toward Artificial Nucleosides



Under N_2, 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.), $Pd(OAc)_2$ (0.01mmol, 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 Et_3N) to give **4a** and **4b**.

6. Characterization Data for the Products

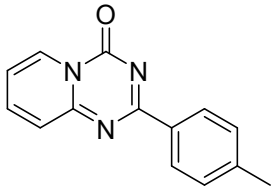
2-Phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2a)[3]:



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2a** (18.9 mg, 85% yield) as white solid. Mp. 190-191 °C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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.

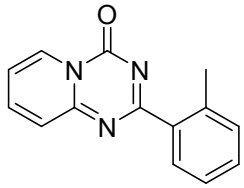
2-(*p*-Tolyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2b):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2b** (19.2 mg, 81% yield) as white solid. Mp. 228-229 °C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{14}H_{12}N_3O^+$ $(M + H)^+$ 238.0975, found 238.0976.

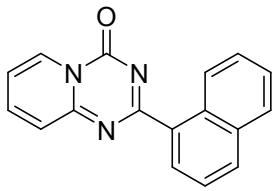
2-(*o*-Tolyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2c):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2c** (20.0 mg, 84% yield) as white solid. Mp. 164-166 °C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.1, 155.1, 150.1, 141.6, 138.5, 136.3, 131.5, 130.7, 129.7,125.8, 125.3, 117.9, 21.6; HRMS (ESI) m/z calcd for $C_{14}H_{12}N_3O^+$ $(M + H)^+$ 238.0975, found 238.0980.

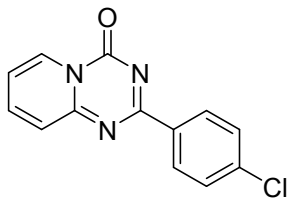
2-(Naphthalen-1-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2d):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2d** (19.7 mg, 72% yield) as white solid. Mp. 171-173 °C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{17}H_{12}N_3O^+$ $(M + H)^+$ 274.0975, found 274.0977.

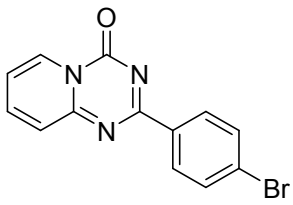
2-(4-Chlorophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2e):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2e** (21.3 mg, 83% yield) as white solid. Mp. > 250 °C.

^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{13}H_9ClN_3O^+$ $(M + H)^+$ 258.0429, found 258.0432.

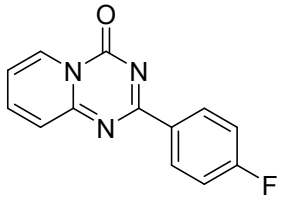
2-(4-Bromophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2f):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2f** (26.0 mg, 86% yield) as white solid. Mp. > 250 °C.

^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{13}H_9BrN_3O^+$ $(M + H)^+$ 301.9924, found 301.9924.

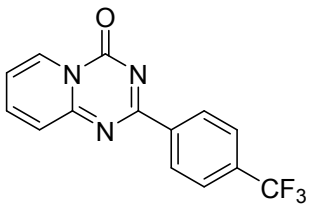
2-(4-Fluorophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2g):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2g** (16.9 mg, 70% yield) as white solid. Mp. 232-234 °C.

^1H NMR (DMSO-d_6, 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, 1H, J = 8.7 Hz), 7.60 (t, 1H, J = 6.8 Hz), 7.41 (t, 2H, J = 8.7 Hz); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 167.5, 165.8 (d, $J_{C\text{-}F}$ = 249.0 Hz), 156.1, 151.5, 144.2, 133.5 (d, $J_{C\text{-}F}$ = 2.3 Hz), 132.3 (d, $J_{C\text{-}F}$ = 9.0 Hz), 131.0, 125.8, 119.9, 116.6 (d, $J_{C\text{-}F}$ = 21.8 Hz); HRMS (ESI) m/z calcd for $C_{13}H_9FN_3O^+$ $(M + H)^+$ 242.0724, found 242.0726.

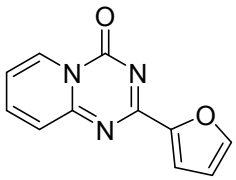
2-(4-(Trifluoromethyl)phenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2h):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2h** (21.8 mg, 75% yield) as white solid. Mp. 169-172 °C.

^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 155.5, 151.1, 142.0, 139.1, 133.7 (q, $J_{C\text{-}F}$ = 32.0 Hz), 130.0, 129.7, 125.6, 125.2 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.9 (q, $J_{C\text{-}F}$ = 271.0 Hz), 118.3; HRMS (ESI) m/z calcd for $C_{14}H_9F_3N_3O^+$ $(M + H)^+$ 292.0692, found 292.0692.

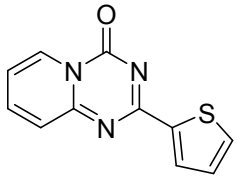
2-(Furan-2-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2i):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2i** (15.1 mg, 71% yield) as white solid. Mp. 209-210 ^oC.

^1H NMR ($CDCl_3$, 400 MHz): δ 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): δ 161.3, 155.7, 150.50, 150.47, 147.0, 142.0, 130.0, 125.1, 118.2, 117.7, 112.8; HRMS (ESI) m/z calcd for $C_{11}H_8N_3O_2^+$ $(M + H)^+$ 214.0611, found 214.0613.

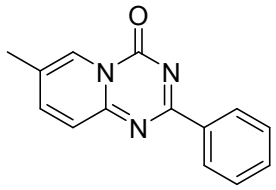
2-(Thiophen-2-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2j):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2j** (17.6 mg, 77% yield) as white solid. Mp. 192-193 ^oC.

^1H NMR ($CDCl_3$, 400 MHz): δ 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): δ 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 $C_{11}H_8N_3OS^+$ $(M + H)^+$ 230.0383, found 230.0385.

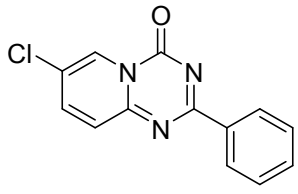
7-Methyl-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2k):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2k** (19.4 mg, 82% yield) as white solid. Mp. 200-201 ^oC.

^1H NMR ($CDCl_3$, 400 MHz): δ 8.88 (s, 1H), 8.54 (d, J = 7.9 Hz, 2H), 7.85 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.9 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): δ 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 $C_{14}H_{12}N_3O^+$ $(M + H)^+$ 238.0975, found 238.0980.

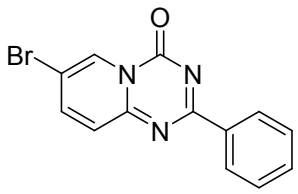
7-Chloro-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2l):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et_3N) give **2l** (18.0 mg, 70% yield) as yellow solid. Mp. 232-234 ^oC.

^1H NMR ($CDCl_3$, 400 MHz) δ 9.09 (s, 1H), 8.56 (d, J = 7.9 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) δ 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 $C_{13}H_9ClN_3O^+$ $(M + H)^+$ 258.0429, found 258.0436.

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

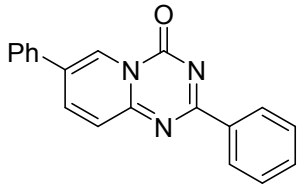


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et_3N) give **2m** (17.8 mg, 59% yield) as yellow solid. Mp. 242-244 ^oC.

^1H NMR ($CDCl_3$, 400 MHz) δ 9.20 (s, 1H), 8.56 (d, J = 7.7

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); ^{13}C NMR ($CDCl_3$, 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 $C_{13}H_9BrN_3O^+$ $(M + H)^+$ 301.9924, found 301.9921.

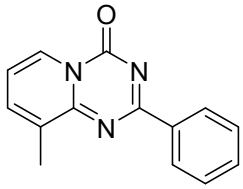
2,7-Diphenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2n):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8 + 0.1% of Et_3N) give **2n** (13.7 mg, 46% yield) as yellow solid. Mp. 245-247 ^{o}C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{19}H_{14}N_3O^+$ $(M + H)^+$ 300.1131, found 300.1133.

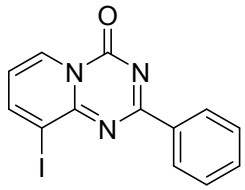
9-Methyl-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2o):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2o** (20.9 mg, 88% yield) as white solid. Mp. 171-174 ^{o}C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{14}H_{12}N_3O^+$ $(M + H)^+$ 238.0975, found 238.0982.

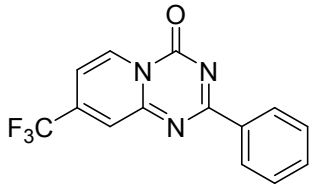
9-Iodo-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2p):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2p** (20.2 mg, 58% yield) as white solid. Mp. 214-215 ^{o}C.

^{1}H NMR ($CDCl_3$, 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), 7.59-7.56 (m, 1H), 7.52-7.48 (m, 2H), 7.03 (t, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 153.9, 151.7, 151.2, 135.5, 133.1, 130.3, 130.0, 128.5, 118.1, 96.7; HRMS (ESI) m/z calcd for $C_{13}H_9IN_3O^+$ $(M + H)^+$ 349.9785, found 349.9783.

2-Phenyl-8-(trifluoromethyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2q):

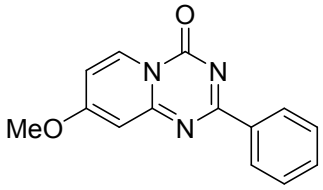


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2q** (18.3 mg, 63% yield) as white solid. Mp. 181-183 ^{o}C.

^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.3, 155.4, 150.4, 142.2 (q, J_{C-F} = 36.0 Hz), 135.0, 133.2, 131.6, 129.7, 128.5,

123.3 (q, $J_{C\text{-}F}$ = 5.0 Hz), 121.3 (q, $J_{C\text{-}F}$ = 273.0 Hz), 112.5 (q, $J_{C\text{-}F}$ = 3.0 Hz); HRMS (ESI) m/z calcd for $C_{14}H_9F_3N_3O^+$ $(M + H)^+$ 292.0692, found 292.0699.

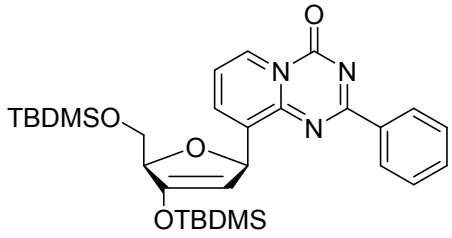
8-Methoxy-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2r):



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3 + 0.1% of Et_3N) give **2r** (17.7 mg, 70% yield) as white solid. Mp. 221-223 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 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): δ 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 $C_{14}H_{12}N_3O_2^+$ $(M + H)^+$ 254.0924, found 254.0934.

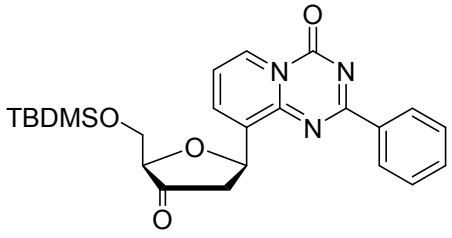
9-((2*R*,5*R*)-4-((*tert*-butyldimethylsilyl)oxy)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)-2,5-dihydrofuran-2-yl)-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (4a):



Flash column chromatography on a silica gel (ethyl acetate: hexane, 1: 3 + 0.1% of Et_3N) give **4a** (16.0 mg, 31% yield) as white solid. Mp. 158-160 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 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), 6.49 (s, 1H), 5.19 (s, 1H), 4.71 (s, 1H), 3.98 (d, J = 11.2 Hz, 1H), 3.84 (d, J = 10.7 Hz, 1H), 0.94 (s, 9H), 0.88 (s, 9H), 0.24 (s, 3H), 0.15 (s, 3H), 0.10 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 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, 84.3, 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 $C_{30}H_{44}N_3O_4Si_2^+$ $(M + H)^+$ 566.2865, found 566.2905.

9-((2*R*,5*R*)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-oxotetrahydrofuran-2-yl)-2-phenyl-4*H*-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_3N) give **4b** (12.7 mg, 28% yield) as yellow oil.

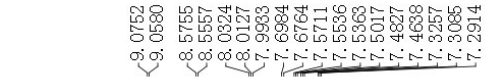
^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.05 (dd, J = 1.3, 6.9 Hz, 1H), 8.53-8.51 (m, 3H), 7.59-7.56 (m, 1H), 7.51-7.48 (m, 2H), 7.37 (t, J = 7.1 Hz, 1H), 5.95-5.92 (m, 1H), 4.21 (t, J = 2.3 Hz, 1H), 4.08-4.00 (m, 2H), 3.45-3.40 (m, 1H), 2.33-2.27 (m, 1H), 0.83 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 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 $C_{24}H_{30}N_3O_4Si^+$ $(M + H)^+$ 452.2000, found 452.2007.

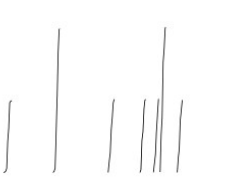
7. References

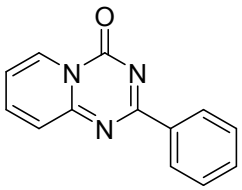
1. Z.-S. Zheng, S.-Y. Ma, L.-L. Tang, D. Zhang-Negrerie, Y.-F. Du and K. Zhao, *J. Org. Chem.,* 2014, **79**, 4687.
2. N. Gaß and H. A. Wagenknecht, *Eur. J. Org. Chem.,* 2015, **2015**, 6661.
3. A. S. Kiselyov and L. Strekowski, *Tetrahedron Lett.,* 1994, **35**, 207.

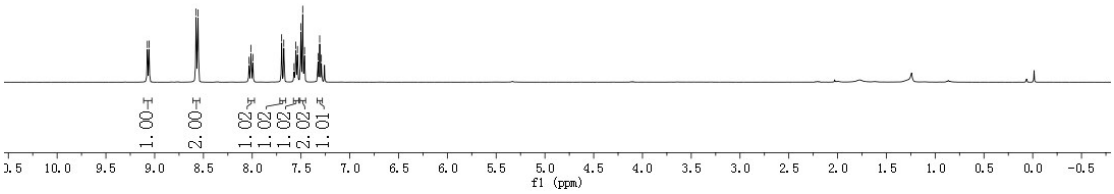
8. Copies of the ^{1}H NMR and ^{13}C NMR Spectra

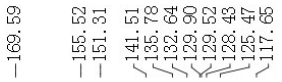
2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2a)

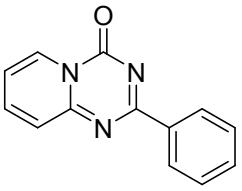


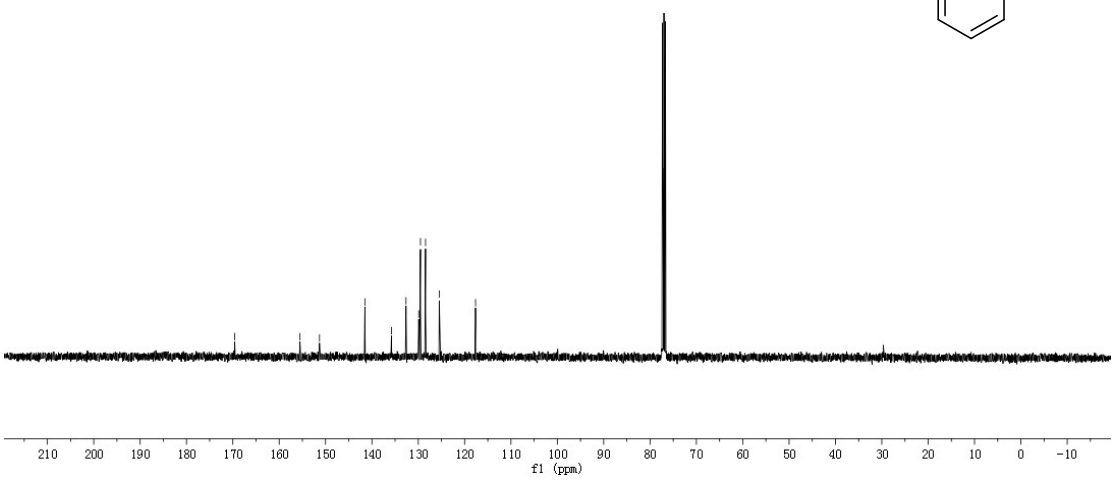




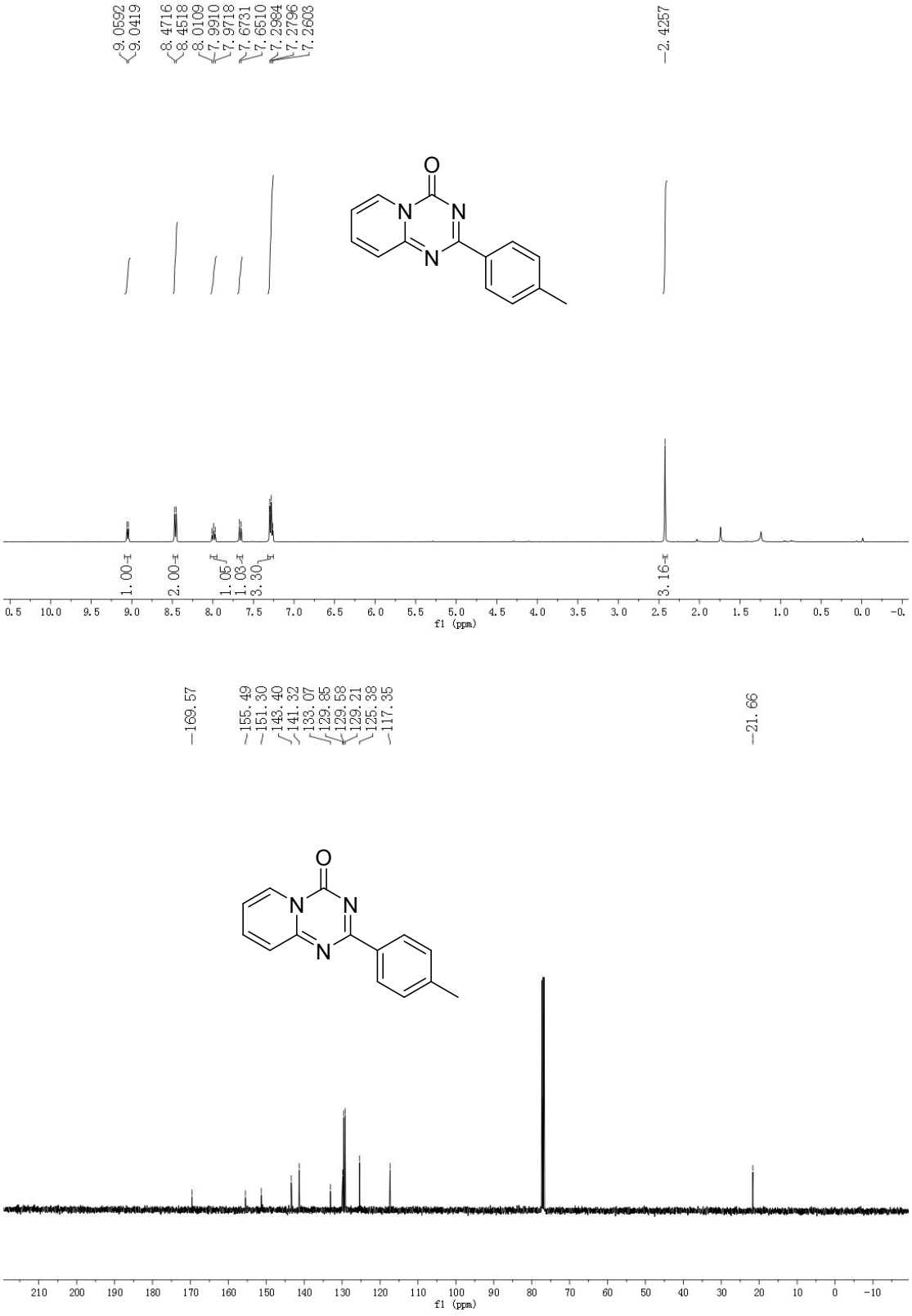




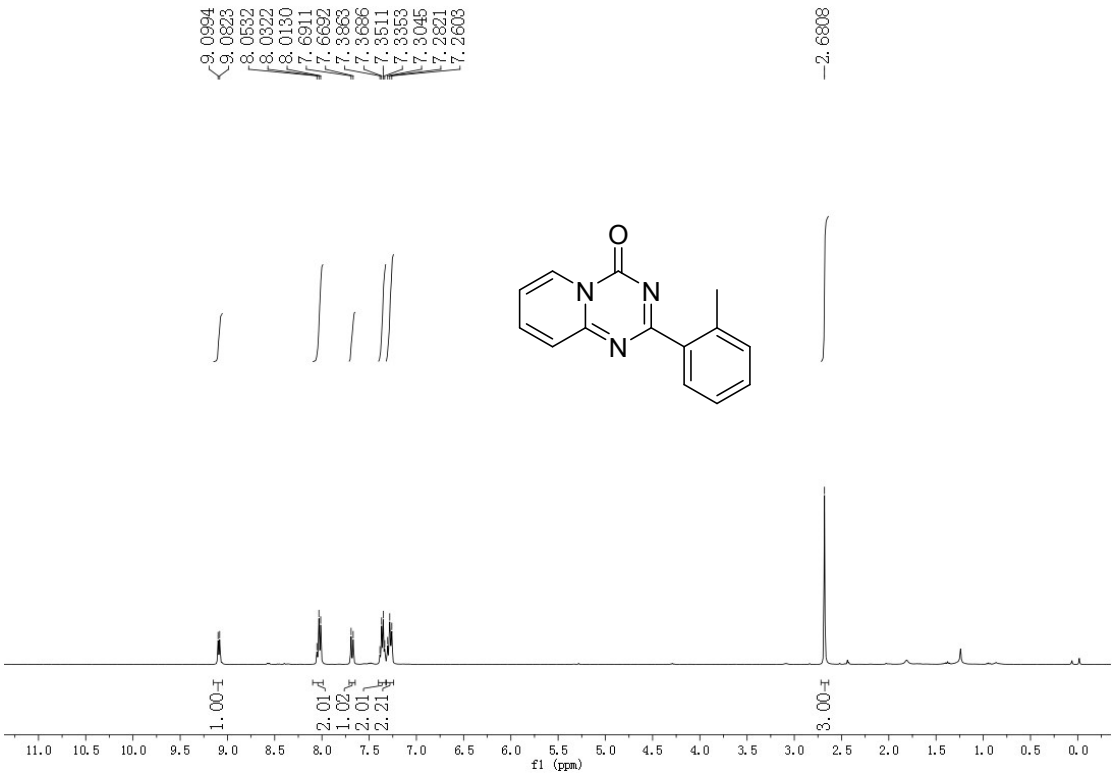


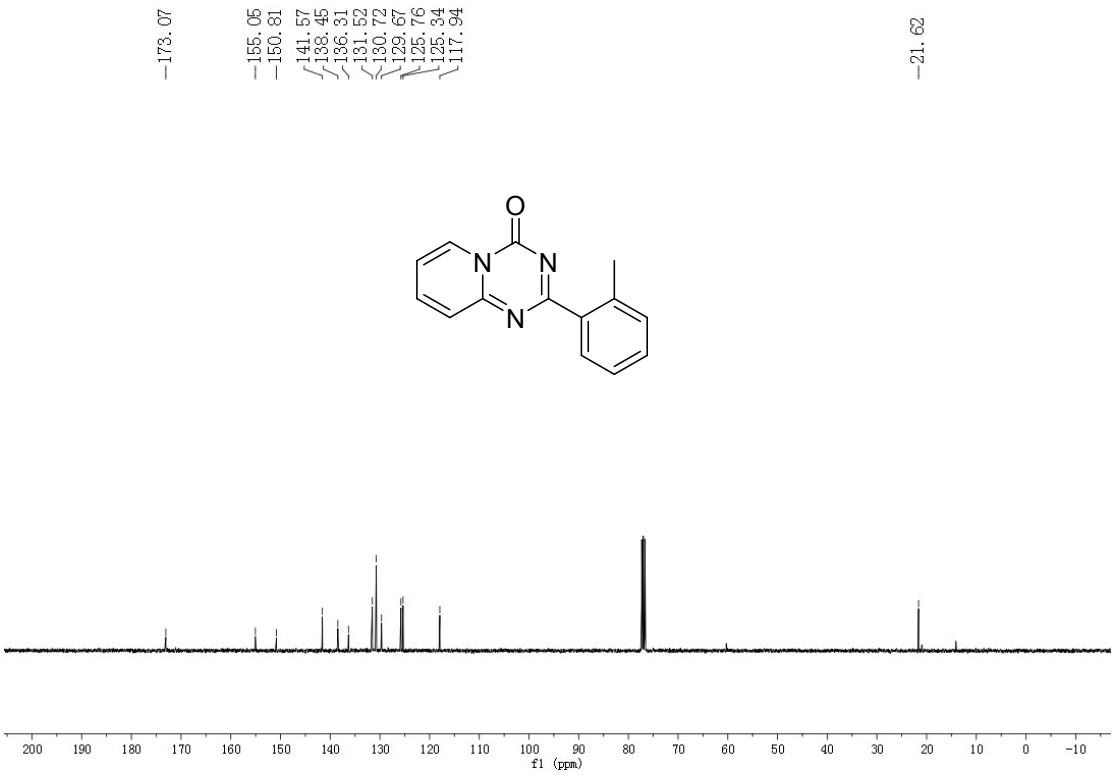


2-(*p*-tolyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2b)

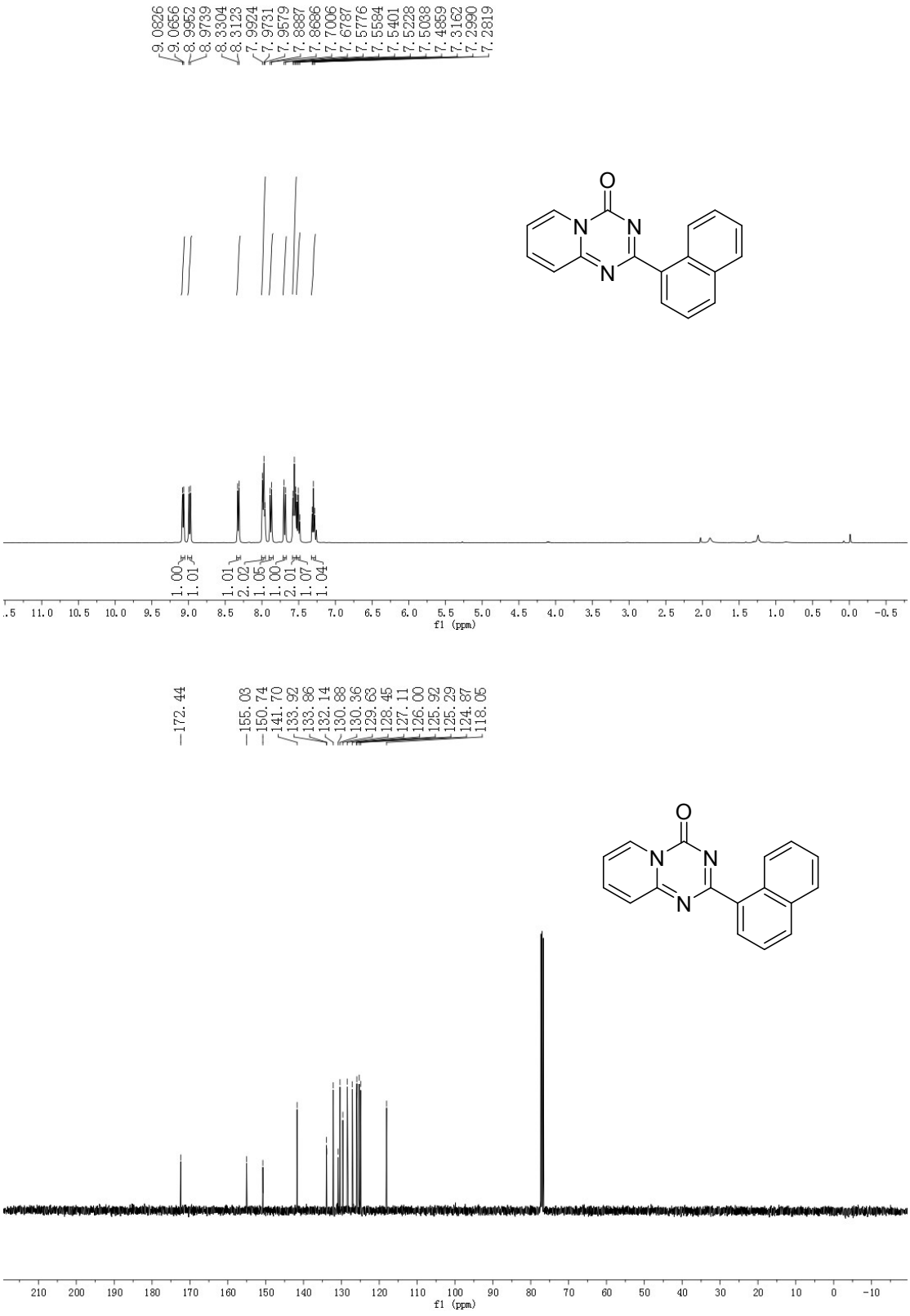


2-(*o*-tolyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2c)

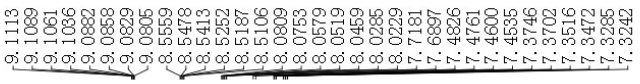


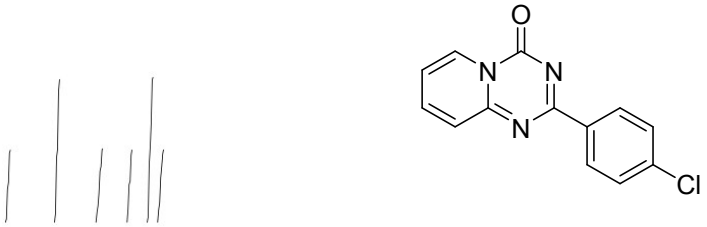


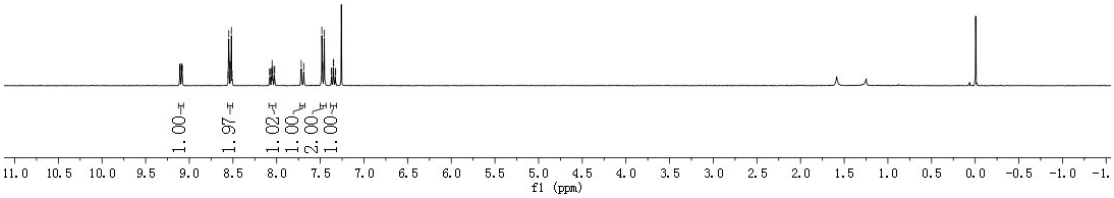
2-(naphthalen-1-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2d)

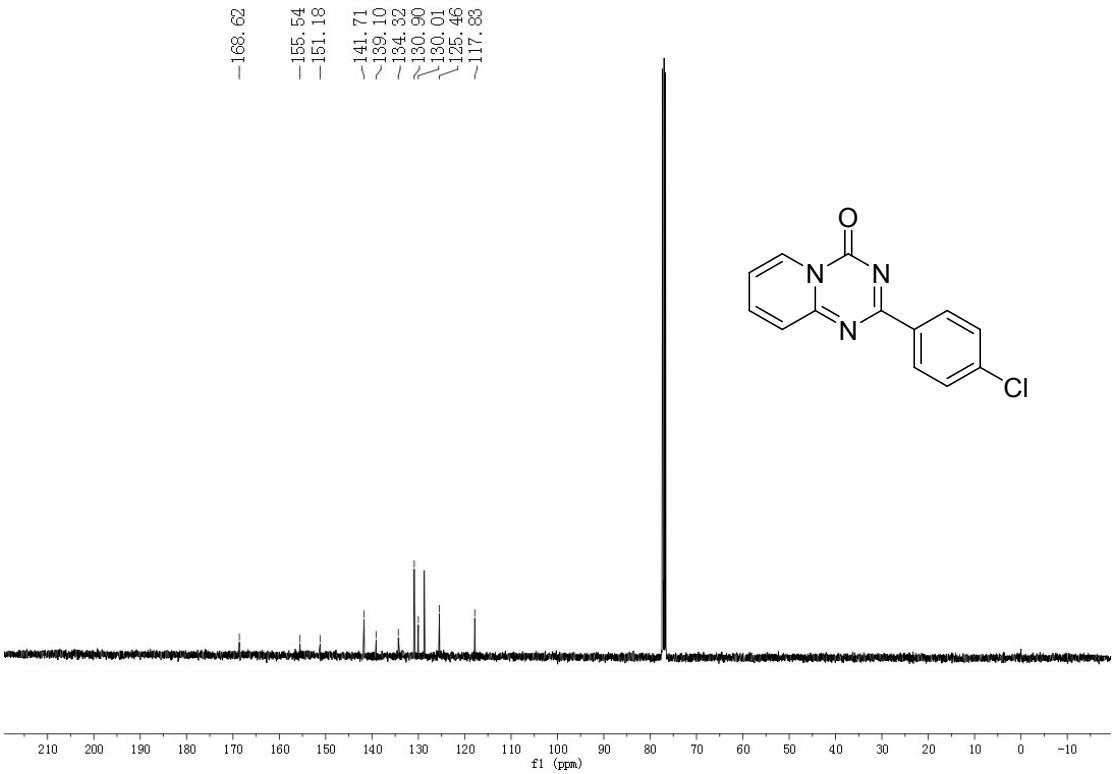


2-(4-chlorophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2e)

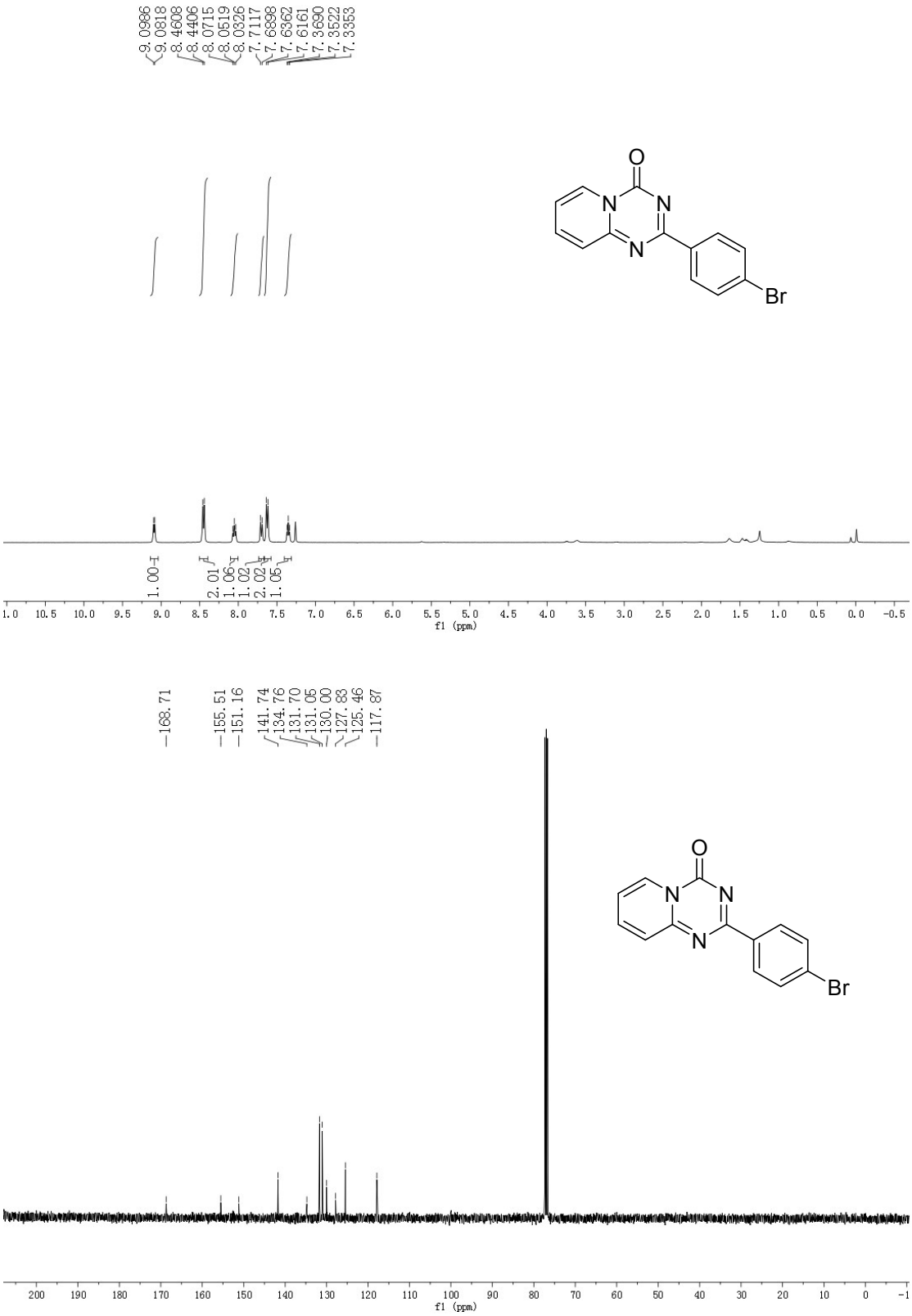




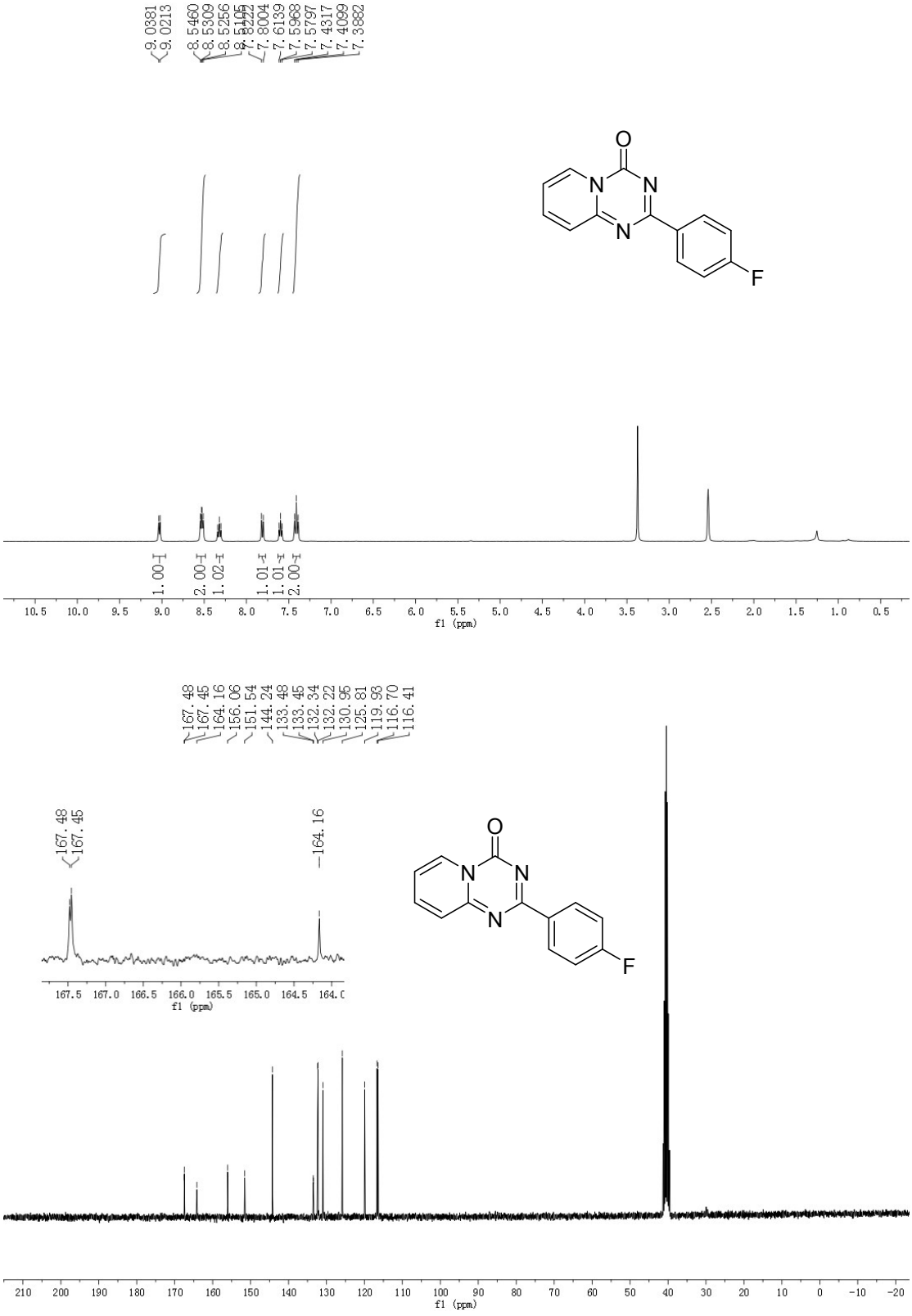




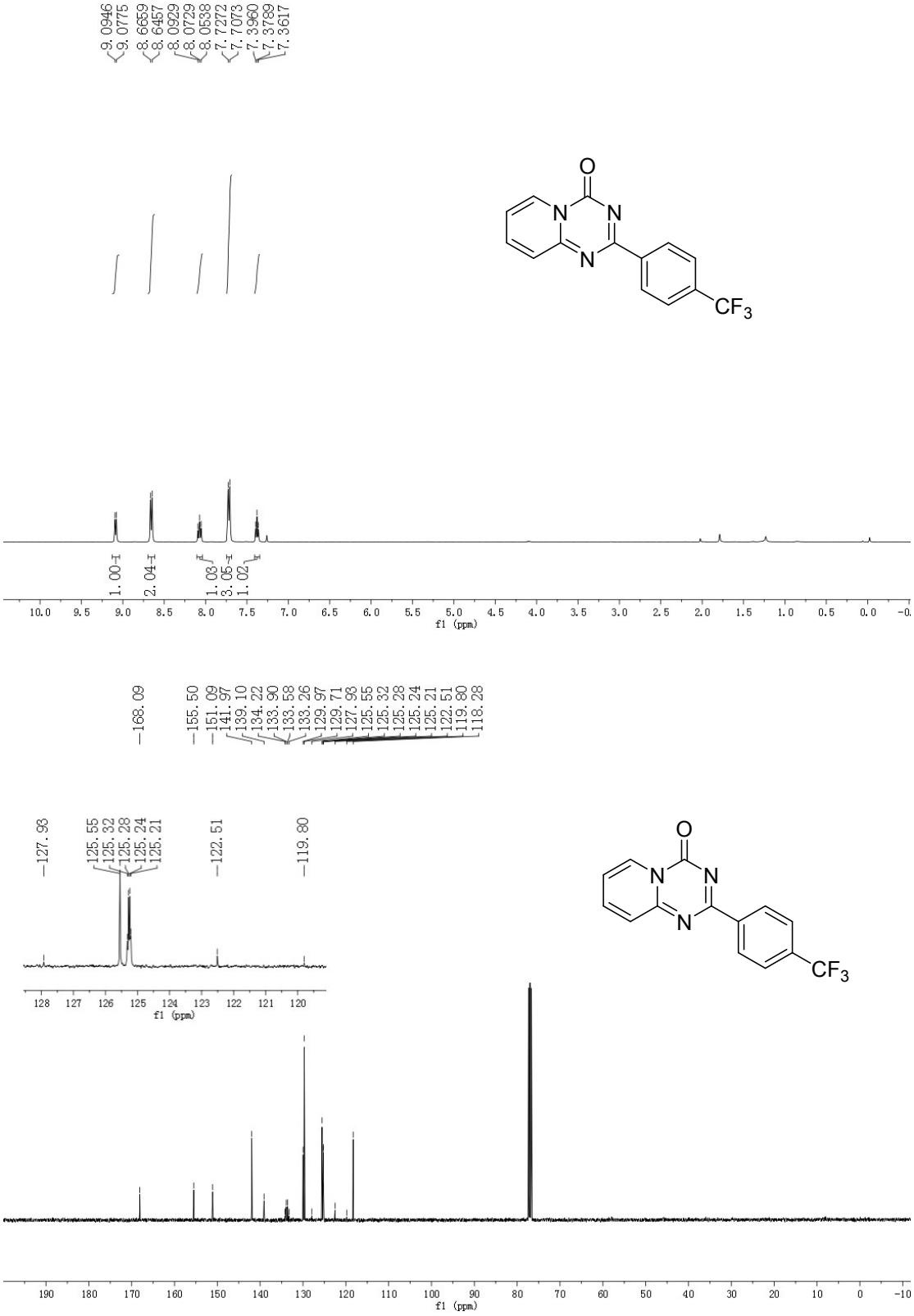
2-(4-bromophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2f)



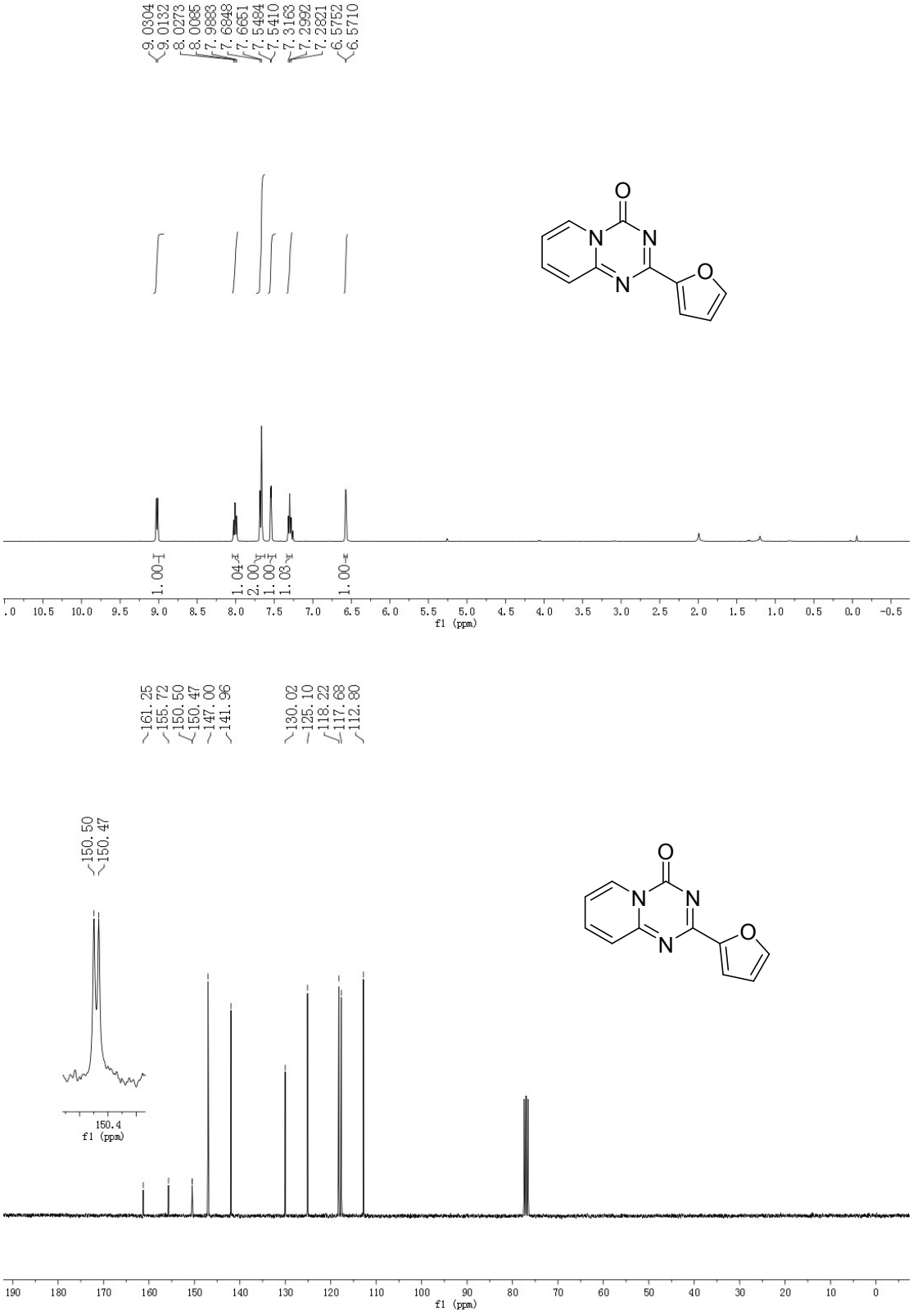
2-(4-fluorophenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2g)



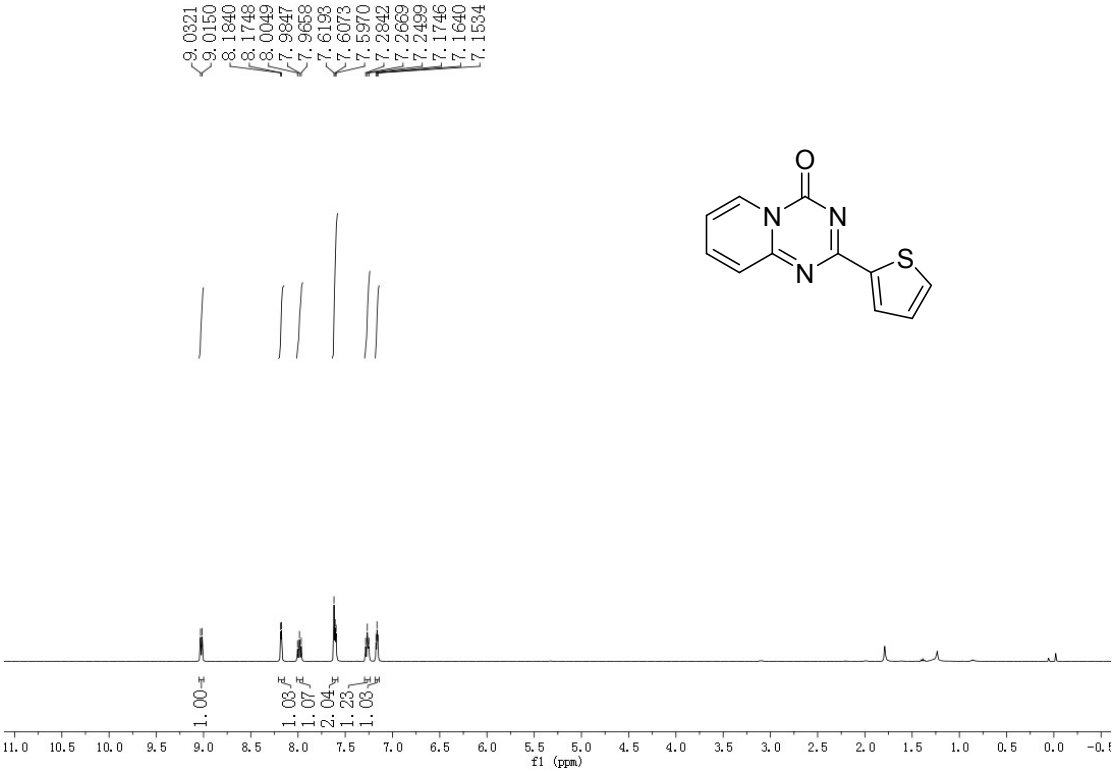
2-(4-(trifluoromethyl)phenyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2h)

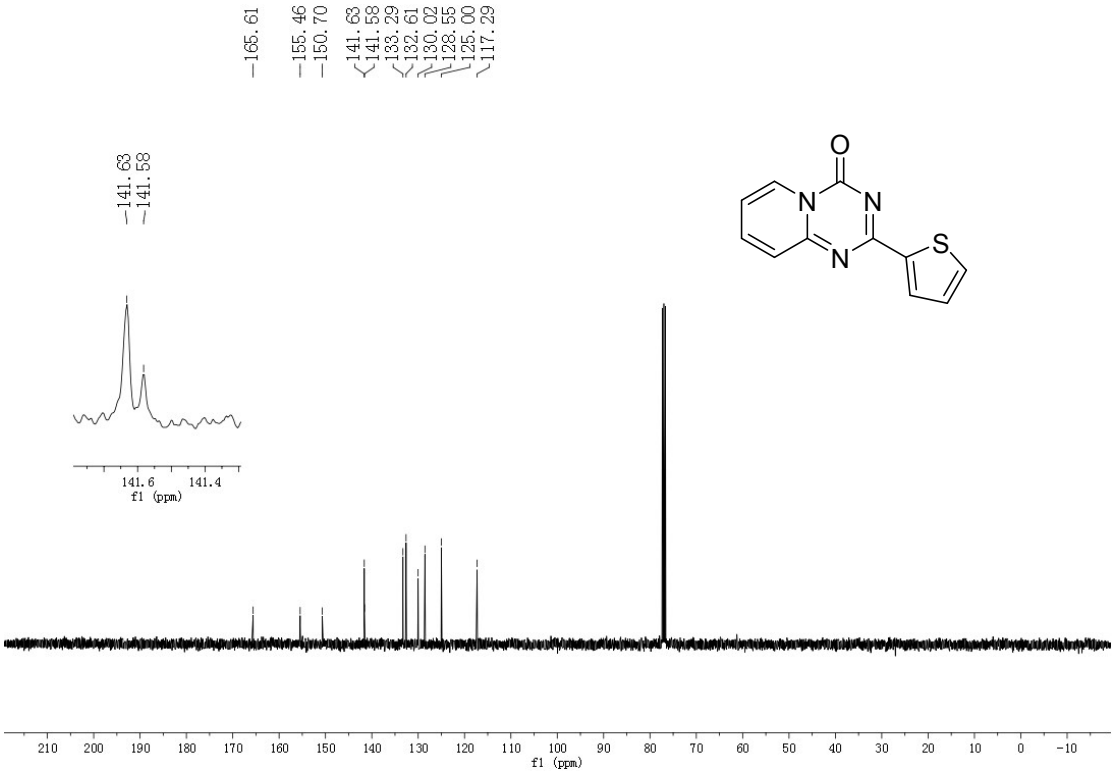


2-(furan-2-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2i)

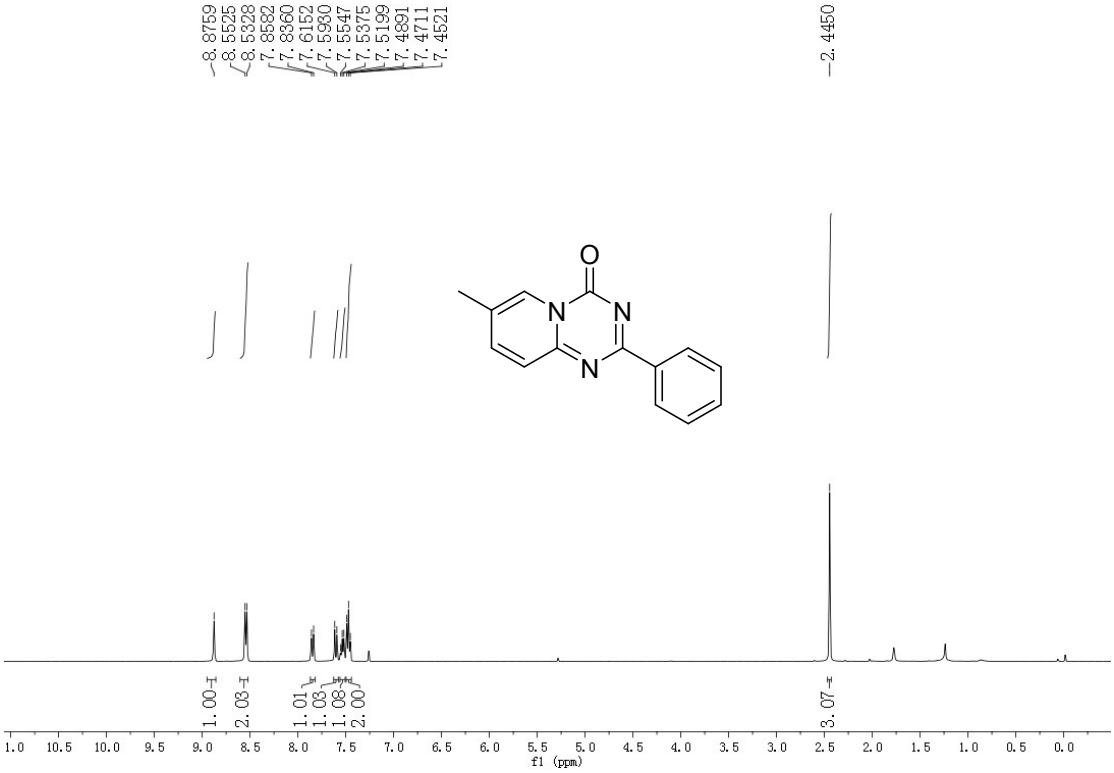


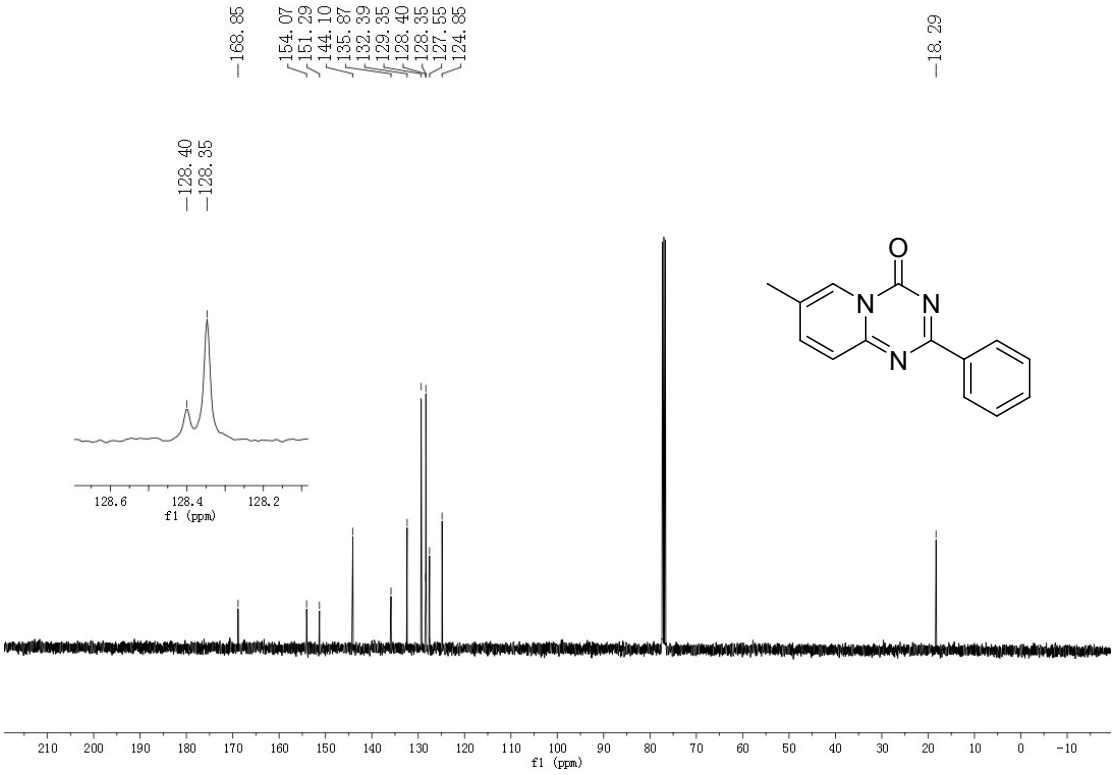
2-(thiophen-2-yl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2j)



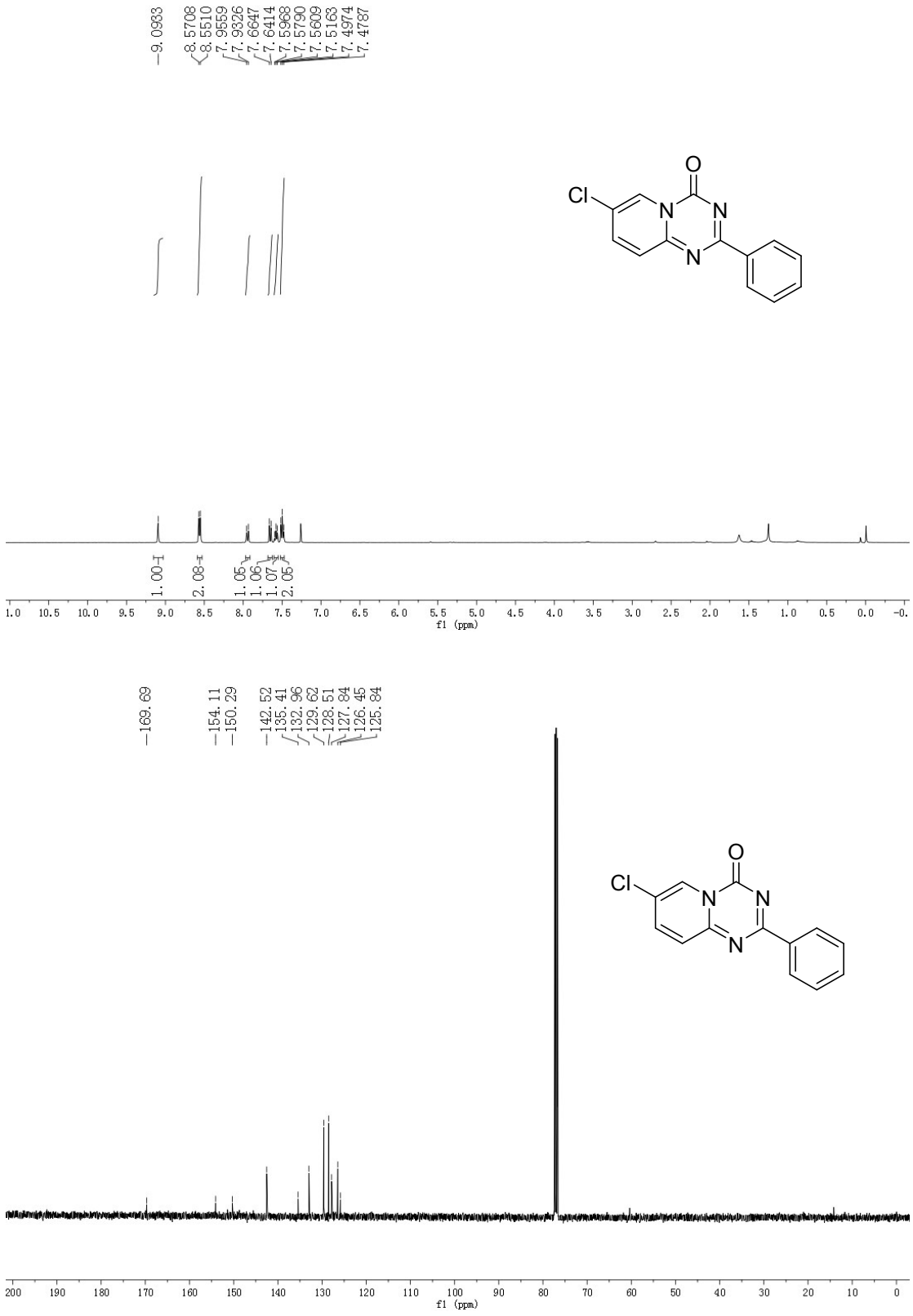


7-methyl-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2k)

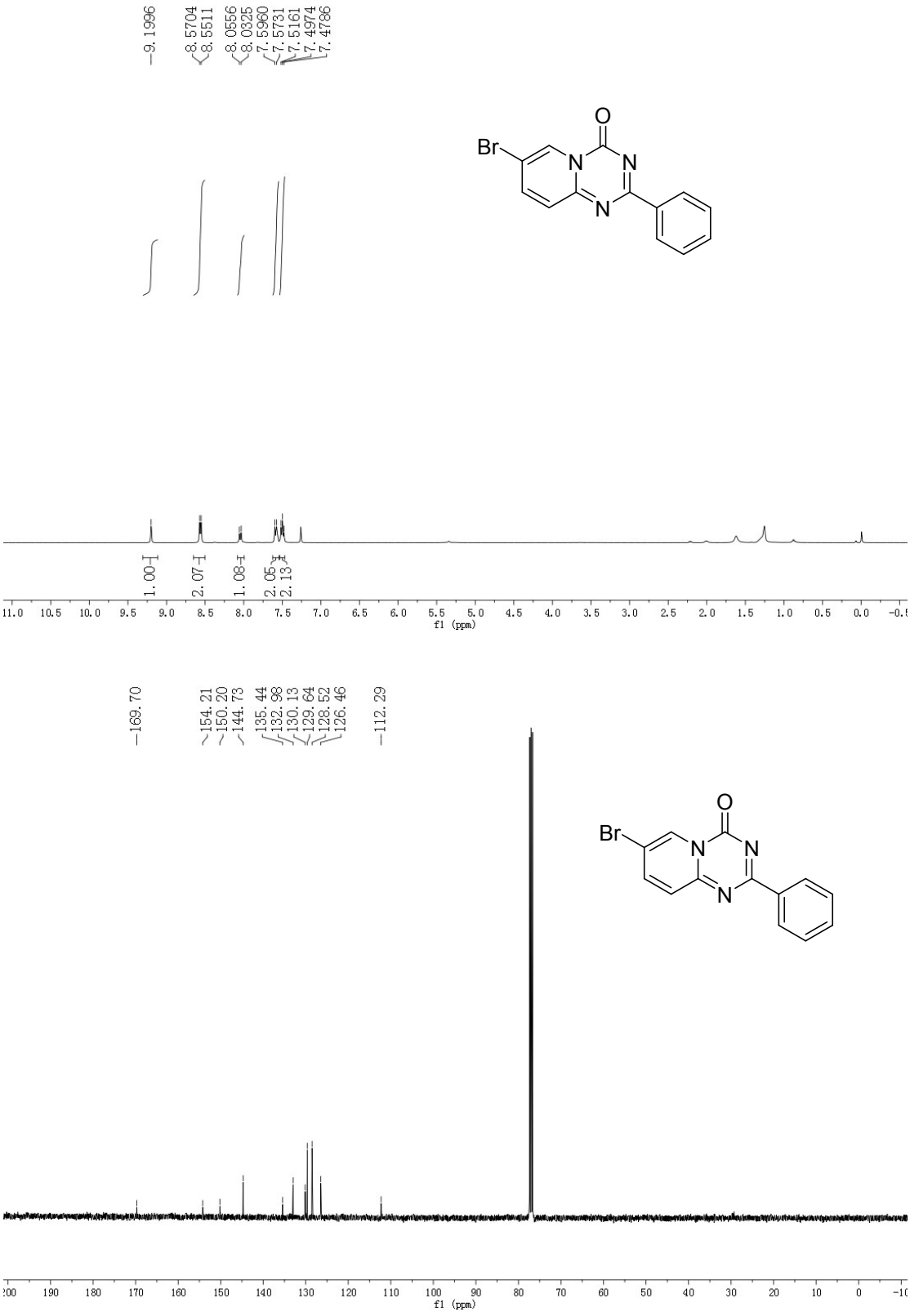




7-chloro-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2l):

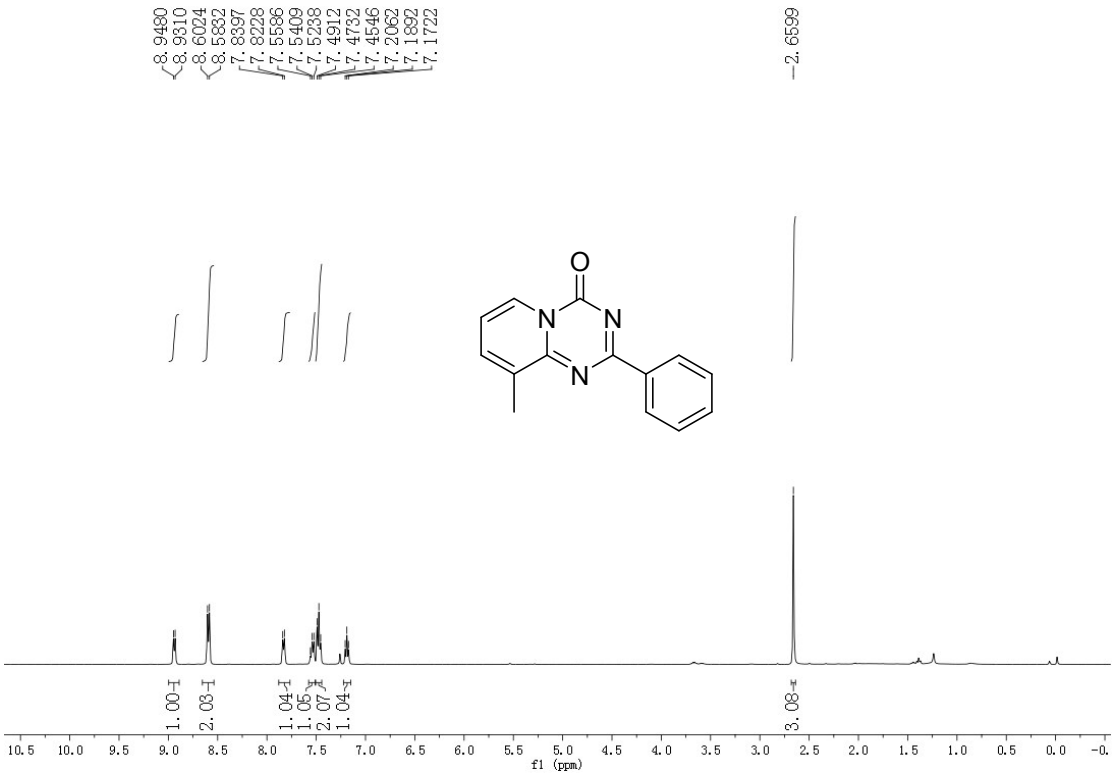


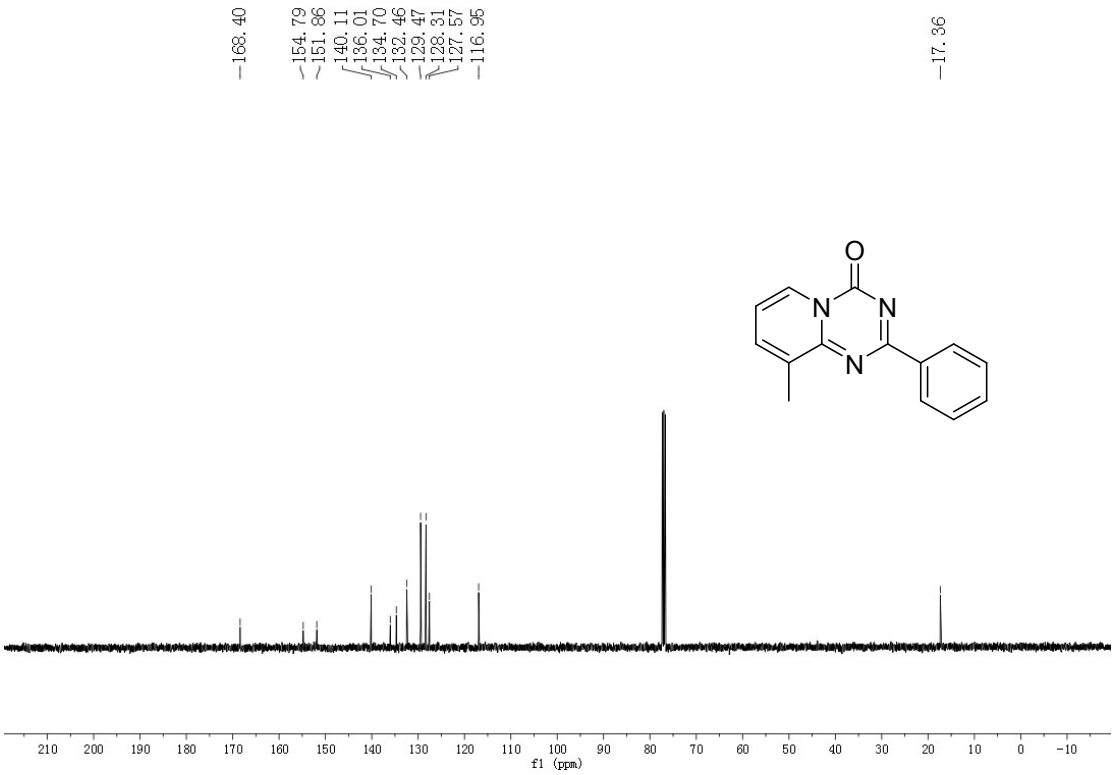
7-bromo-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2m)



2,7-diphenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2n)

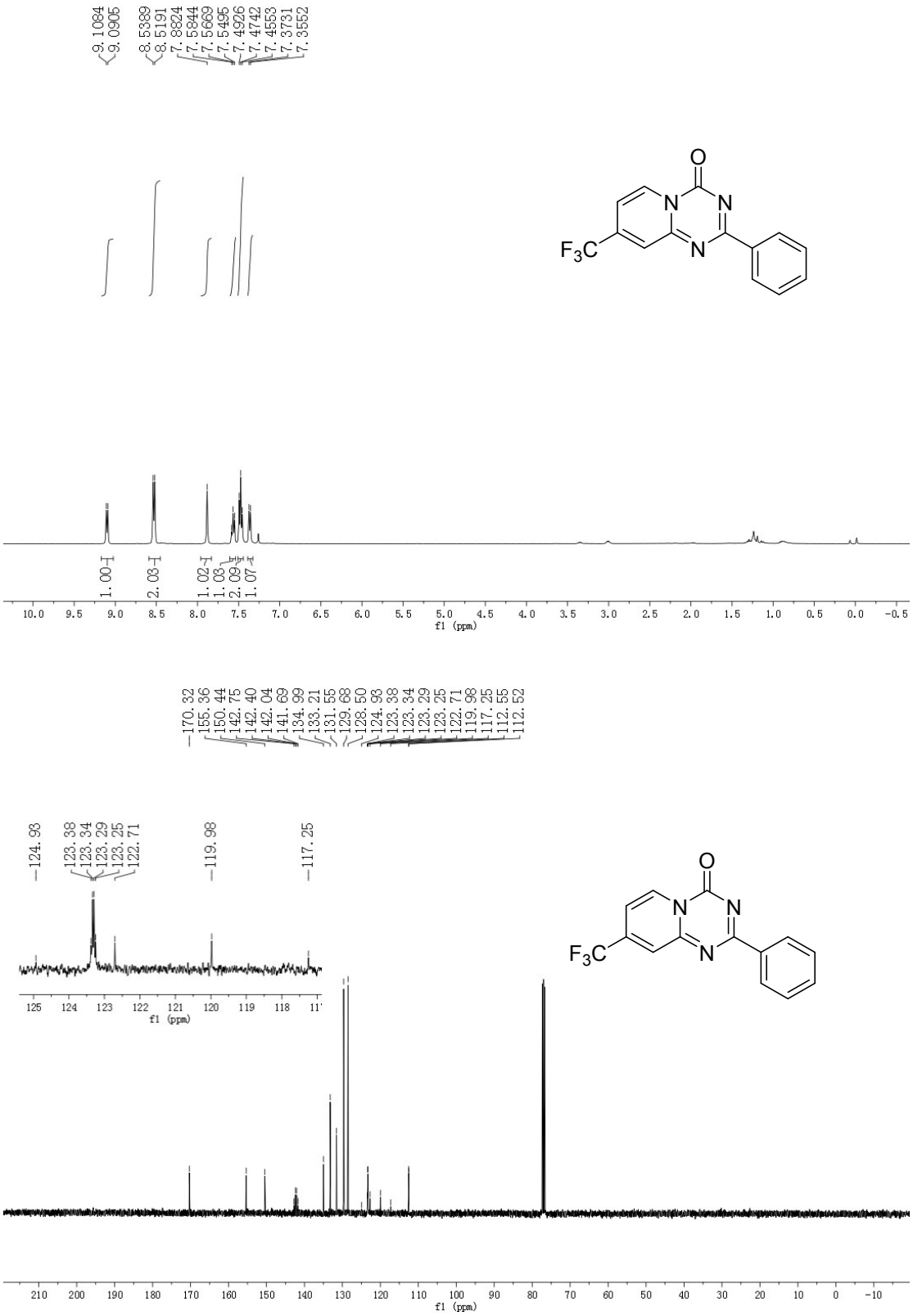
7-methyl-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2o)



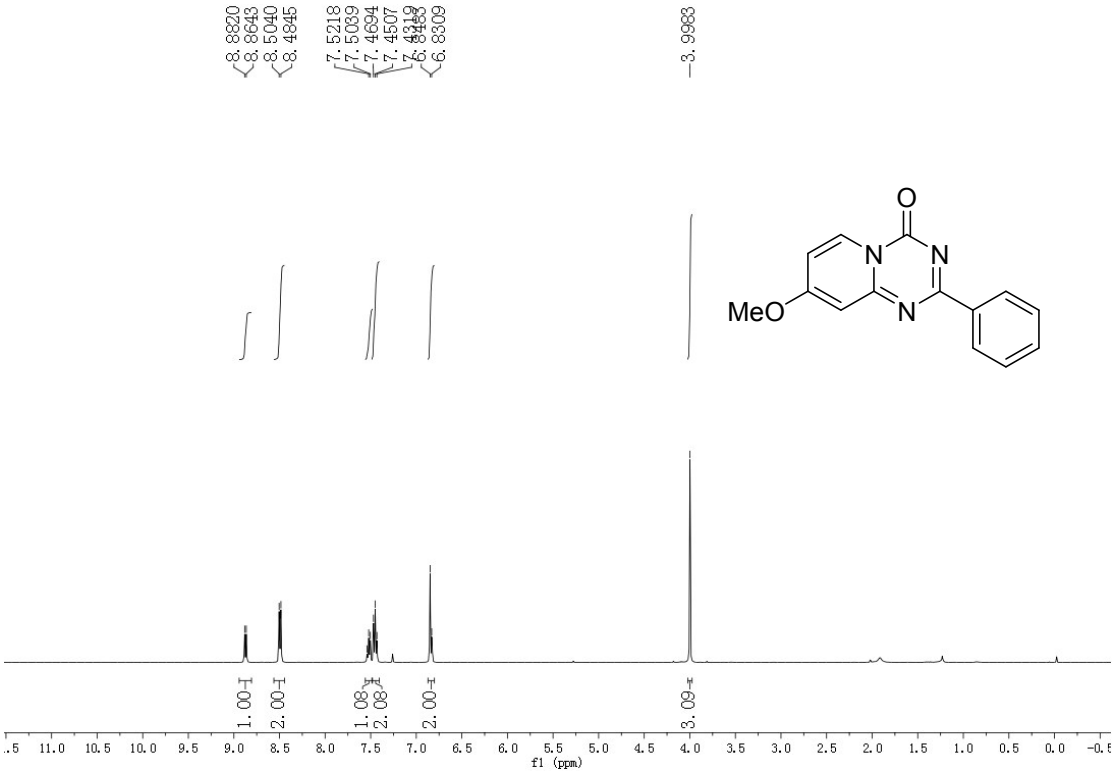


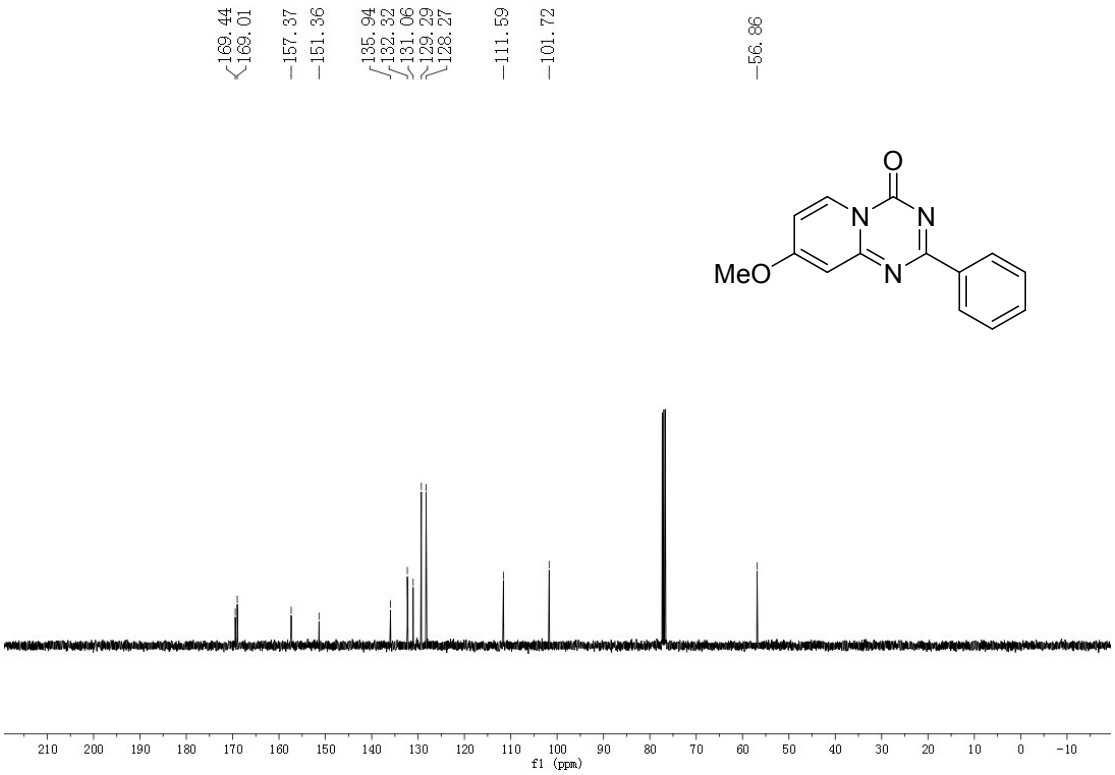
9-iodo-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2p)

2-phenyl-8-(trifluoromethyl)-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2q)

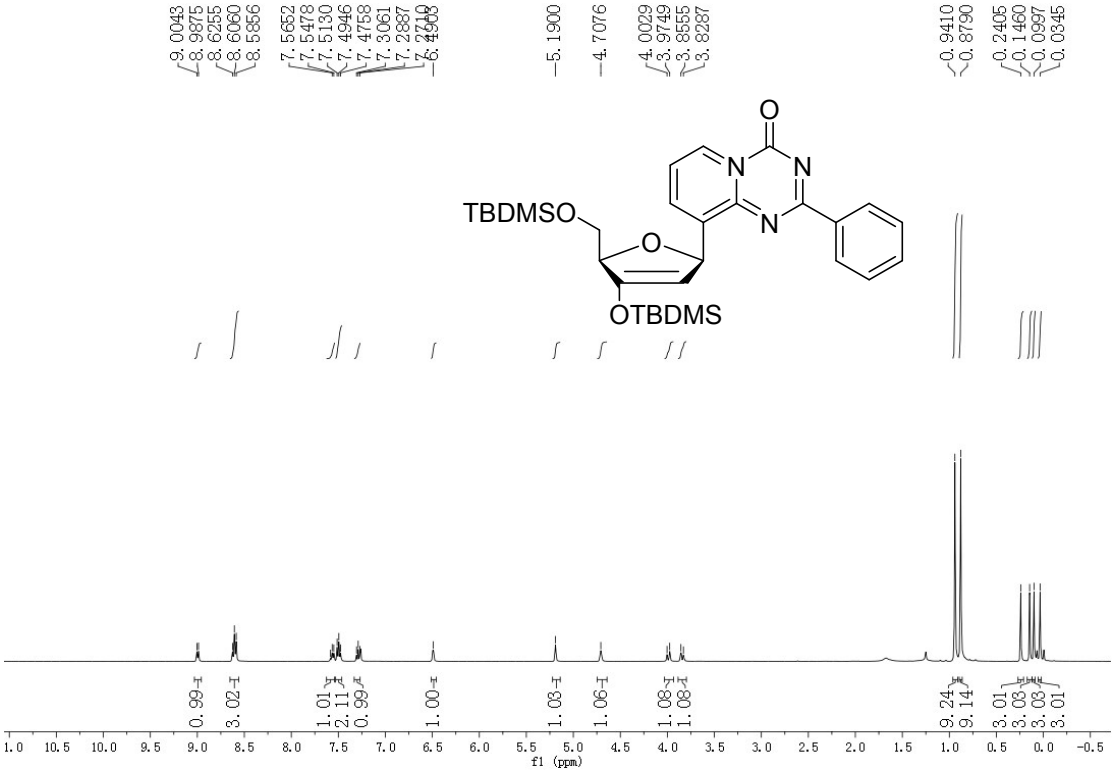


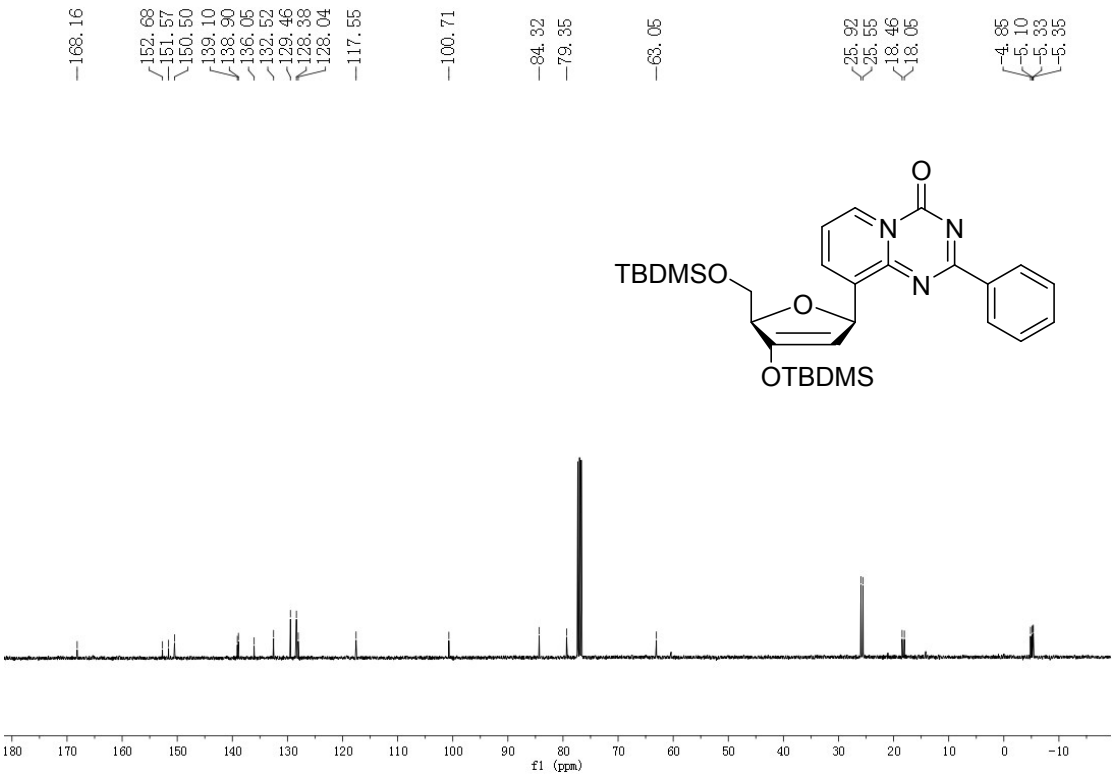
8-methoxy-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (2r)





9-((2*R*,5*R*)-4-((*tert*-butyldimethylsilyl)oxy)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)-2,5-dihydrofuran-2-yl)-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (4a)





9-((2*R*,5*R*)-5-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-oxotetrahydrofuran-2-yl)-2-phenyl-4*H*-pyrido[1,2-*a*][1,3,5]triazin-4-one (4b)