Supporting Information

Photoinduced direct C-H cyanoalkylation of azauracils via electron donoracceptor complex activation

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1. General Information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in preheated glassware under a nitrogen atmosphere using standard Schlenk techniques. LED lights were purchased from Shenzhen Xinxingyuan Co., Ltd. (20 W/5313 A)- 395 nm with 3 cm from the reaction tube made up of borosilicate glass without any filter. All reactions involving heating were carried out on the heated magnetic stirrer from DALB: model MS-H280-Pro. All reagents were weighed and handled in air at room temperature. All chemical reagents were purchased from Energy Chemical and aladdin and used without further purification.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Ocean Chemical Co., Ltd silica gel plates (Silica gel GF254). Visualisation was conducted under ultraviolet ($\lambda = 254$ nm). Flash column chromatography was performed using 200-300 mesh silica gel.

¹H NMR and ¹³C NMR: Spectra were recorded on Bruker spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl₃. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: CHCl₃ (δ = 7.26 for ¹H NMR and δ = 77.16 for ¹³C NMR). Data are reported as follows: chemical shift δ /ppm, integration (¹H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or combinations thereof, coupling constants J in Hz, assignment.

High Resolution Mass Spectrometry (HRMS): All were recorded on Thermo Q-Exactive instrument (quadrupole mass analyzer) using a positive electrospray ionization (ESI). Measured values were reported to 4 decimal places of the calculated value. The calculated values were based on the most abundant isotope.

UV-vis spectrophotometer: UV-vis absorption spectra were recorded on Shimadzu UV-1900i in DMSO.

Gas Chromatography-Mass Spectrometry (GC-MS): GC-MS were determined by Thermo Scientific Trace1300-ISQ7000.

Melting points (MP) were determined by WRS-1B.

Electrochemical workstation: CHI6034E Apparatuses.

2. Complete Optimization Table

Table S1. Screening of the reaction conditions

	+ NOT CF3 Purple light (395 nm) DMSO, N ₂ , 35 °C, 16 h	Bn N N CN
1a	2a	3aa
entry ^a	variation from standard condition	yield $(\%)^b$
1	None	94
2	425 nm instead of 395 nm	42
3	455 nm instead of 395 nm	Trace
4	DMA instead of DMSO	80
5	DMF instead of DMSO	44
6	H ₂ O instead of DMSO	0
7	MeCN instead of DMSO	0
8	DMC instead of DMSO	0
9	1.0 eq. 2a was used	79
10	1.2 eq. 2a was used	80
11	In the dark	0
12	Under air	0

^{*a*} Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), in DMSO (3.0 mL) at 35 °C for 16 h under the irradiation of purple LED (395 nm, 20 W) in the N₂ atmosphere. ^{*b*} isolated yields.

3. Starting Material Preparation

3.1 General procedure for the synthesis of azauracils



Scheme S1. Synthesis of for azauracils

Alkyl halide (3.6 mmol, 0.9 equiv.) was added dropwise to a stirring solution of 6-azauracil (4.0 mmol, 1.0 equiv.), K_2CO_3 (2.0 mmol, 0.5 equiv.) in DMF (40 mL). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was quenched with saturated Na₂CO₃ solution and extracted with DCM for three times. The organic layers were combined, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give to afford the corresponding *N*-2-alkyl-6-azauracils.

Alkyl halide (2.0 mmol, 1.0 equiv.) was added dropwise to a stirring solution of *N*-1- alkyl-6-azauracil (2.0 mmol, 1.0 equiv.), K_2CO_3 (1.0 mmol, 0.5 equiv.) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was quenched with saturated Na₂CO₃ solution and extracted with DCM for three times. The organic layers were combined, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using petroleum ether/ethyl acetate as eluent to give to afford the corresponding azauracils.¹

3.2 General procedure for the synthesis of cycloketone oxime esters



Scheme S2. Synthesis for cyclobutanone oxime ester

To a stirred solution of cycloketone (1.0 equiv.) in MeOH (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv.) at room temperature. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a mixture of cyclokeone oxime (1.0 equiv.), triethylamine (2.0 equiv.) and CH_2Cl_2 (0.5 M) in a 30 mL two-necked flask was added acyl chloride (1.5 equiv.) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over MgSO₄. The solvent was removed under vacuum and the residue was subjected to column chromatography with EtOAc-hexane as an eluent to give cycloketone oxime esters.²

4. Experimental Procedure

4.1 Representative procedure for the synthesis of products



Scheme S3. Synthesis of cyanoalkylated azauracils

Azauracil **1a** (0.24 mmol, 1.2 equiv.), cyclobutanone oxime ester **2a** (0.2 mmol, 1.0 equiv.) were sequentially added in a pre-dried 25 mL Schlenk tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then dry dimethyl sulfoxide (2.0 mL) was added under the N_2 atmosphere. The resulting reaction mixture was allowed to stir for 16 h at 35 °C under the irradiation of 20 W purple LED light. After completion, the mixture was extracted three times with water and ethyl acetate, organic layers were combined, dried over anhydrous

sodium sulfate, and concentrated under reduced pressure. Using a mixture of petroleum ether and ethyl acetate as eluent, the mixture was purified through silica gel chromatography to obtain the desired product **3aa**.

4.2 Gram-scale synthesis



Scheme S4. Gram-scale synthesis of product 3aa

The mixture of 2,4-dibenzyl-1,2,4-triazine-3,5 (2*H*,4*H*) -dione **1a** (1.056 g, 3.60 mmol, 1.2 equiv.), cyclobutanone oxime ester **2a** (0.771 g, 3.0 mmol, 1.0 equiv.) were added in a predried 100 mL schlenk flask under N₂ atmosphere. The flask was degassed and purged with N₂ three times. Then dry dimethyl sulfoxide (45 mL) was added under the N₂ atmosphere, and the resulting solution was allowed to stir for 72 h at 35 °C under irradiation of 2×20 W blue LED light. After completion, the mixture was extracted three times with water and ethyl acetate, organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Using a mixture of petroleum ether and ethyl acetate as eluent, the mixture was purified through silica gel chromatography to obtain the desired product **3aa** in 75% yield

5. X-ray Crystallography Date of 3ak

The crystal of 3ak was grown in the air by slow evaporation of the solvents (a mixture of *n*-hexane/dichloromethane) at room temperature.



Figure S1. The thermal ellipsoid plot of 3ak.

Table S2.	Crystal	data and	structure	refinement	for	3ak.
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Identification code	2417115
Empirical formula	$C_{21}H_{19}BrN_4O_2$
Formula weight	439.30
Temperature/K	293
Wavelength/Å	0.71073
Crystal system	monoclinic
Space group	P 2 _{1/c}
a (Å)	13.6693(11)
b (Å)	14.0976(9)
c (Å)	11.4593(7)
α (°)	90
β(°)	113.319(8)
γ (°)	90
Volume/ Å ³	2027.9(3)
Ζ	4
$\rho_{calc}g/cm^3$	1.439
μ/mm^{-1}	2.051
F(000)	896.0

6. Mechanistic studies

6.1 GC-MS analysis of the reaction



Azauracil **1a** (0.24 mmol, 1.5 equiv.) and cyclobutanone oxime ester **2a** (0.2 mmol, 1.0 equiv.) were sequentially added in a pre-dried 25 mL Schlenk tube under N₂ atmosphere. The tube was degassed and purged with N₂ three times. Then dry dimethyl sulfoxide (2.0 mL) was added under the N₂ atmosphere. The resulting reaction mixture was allowed to stir for 16 h at 35 °C under the irradiation of 20 W purple LED light. After completion (16 h), The reaction solution was extracted, dried, diluted and detected by GC-MS. The experimental results indicated that trifluoromethyl benzoic acid was indeed formed.



Figure S2. Determination of trifluoromethyl benzoic acid by GC-MS

6.2 Radical trapping experiments



Figure S3. Compound 4 and 5 were detected by HR-MS analysis

6.3 UV-vis absorption experiments

UV-vis spectroscopic measurements were performed in DMSO at 0.1 M concentration for each species.

each species.



Figure S4. UV-vis absorption spectra.

6.4 Light-dark experiment

The mixture of 2,4-dibenzyl-1,2,4-triazine-3,5 (2*H*,4*H*) -dione **1a** (0.24 mmol, 1.2 equiv.), cyclobutanone oxime ester **2a** (0.2 mmol, 1.0 equiv.) were added in a pre-dried 25 mL Schlenk

tube under N_2 atmosphere. The tube was degassed and purged with N_2 three times. Then dry dimethyl sulfoxide (2.0 mL) was added under the N_2 atmosphere. The resulting reaction mixture was allowed to stir at 35 °C under the irradiation of 20 W purple LED light. The reaction was placed in light and dark in every alternative 1 h. After completion, the mixture was extracted three times with water and ethyl acetate, organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Using a mixture of petroleum ether and ethyl acetate as eluent, the mixture was purified through silica gel chromatography to obtain the desired product **3aa**.

Entry	Time (h)	Light Source	Yield (%)
1	2	On	25
2	3	Off	25
3	4	On	38
4	5	Off	38
5	6	On	56
6	7	Off	56
	60 50 (%) 40 Plaix 20 10 0 0 1	dark 2 3 4 5 6 Time (h)	ırk 7

Figure S5. Light-dark experiment

6.5 Quantum yield determination³

Azauracil **1a** (0.24 mmol, 1.2 equiv.), and cyclobutanone oxime ester **2a** (0.2 mmol, 1.0 equiv.) were combined in dimethyl sulfoxide (2.0 mL) under N₂ atmosphere. The reaction mixture was stirred and irradiated ($\lambda = 395$ nm) for 2 h. After irradiation, the solution was measured the unit area photon flux (MQ-500 photosynthetic active radiation meter). And the yield of product was 25% after being irradiated for 2 hours.

$$\phi = \frac{mol \ product}{fiux \cdot S \cdot t}$$

Where, Φ is quantum yield, S (m²) is the irradiation area and t (s) is the photoreaction time. Experiment: the unit photon flux was 123 µmol·s⁻¹·m⁻² (average of three experiments), the irradiation area was 3.38×10^{-4} m², and the product yield was 25% after 2 h (7200 s). Quantum yield calculation:

$$\emptyset = \frac{mol \ product}{fiux \cdot S \cdot t} = \frac{0.1 \times 0.25 \times 10^3}{112 \times 3.38 \times 10^{-4} \times 7200} = 0.0917$$



Figure S6. Placement of 395 nm LED and MQ-500 photosynthetic active radiation meter.



6.6 The experiments of photocurrent and Cyclic voltammetry

Figure S7. Photocurrent and CV experiments at glass carbon as the work electrode, Pt (1.5 \times 1.5 cm²) as the counter electrode, Ag/AgCl as the reference electrode, "Bu₄NBF₄(0.1 M). (a) Photocurrent tests were performed in corresponding reaction solvents, **1a** (0.05 M), **2a** (0.05 M), purple LEDs (390 nm). (b) Cyclic voltammetry, scan rate = 100 mV/s, CH₃CN (20.0 mL), **1a** (0.3 mM), **2a** (0.3 mM).

Potential (V vs. Hg/Hg₂Cl₂/KCl)

6.7 Determination of the binding ratio by Job's plot

Time (s)

Job's plot was performed according to the literature method.⁵ Cyclobutanone oxime **2a** was dissolved in DMSO-*d6* (3.0 mL) to give a stock solution at 0.1 mol/L concentration. Similarly, 2,4-dibenzyl-1,2,4-triazine-3,5 (2*H*,4*H*) -dione **1a** was added to DMSO-*d*₆ (3.0 mL) solution to provide a 0.1 mol/L solution. Then, the solutions of **1a** and **2a** were added to the NMR tube based on the specific ratio in Table. The ¹H (Ar-H) chemical shift of free **2a** solution (0.1 mol/L) is 8.1646 ppm. The job's plot had a maximum when X (**2a**) equals to 0.5, suggesting that the binding stoichiometry between **1a** and **2a** is 1:1.



Figure S8. ¹H NMR shift of 1a with 2a

Table S2. ¹H NMR experimental data for Job's plot

Entry	V (2a , mL)	V (1a , mL)	X	δ(¹ H(Ar-H), ppm)	$\Delta\delta(ppm)$	$\Delta \delta^* X (2a) *10^{-3}$
1	0.45	0.05	0.9	8.1658	0.0010	0.90
2	0.40	0.10	0.8	8.1665	0.0025	2.00
3	0.35	0.15	0.7	8.1676	0.0035	2.45
4	0.30	0.20	0.6	8.1685	0.0046	2.76
5	0.25	0.25	0.5	8.1695	0.0060	3.00
6	0.20	0.30	0.4	8.1703	0.0071	2.84
7	0.15	0.35	0.3	8.1714	0.0083	2.49
8	0.10	0.40	0.2	8.1722	0.0086	1.72
9	0.05	0.45	0.1	8.1731	0.00106	1.06



Figure S9. Job's plot

7. Density Functional Theory Calculations

7.1 Computational details

Gaussian 16 software was used to do theoretical computations. Geometrical optimization was performed at the M062X/6-311+g (d, p) level, and frequency analysis was performed to ensure the complex did not have any imaginary frequencies ^[4]. In the computations, the implicit solvent model (SMD) was utilized using DMSO as the solvent, the temperature was set to 308.15 K, and the dispersion correction was applied with the keyword em = gd3. Calculations using time-dependent density-functional theory were done on the EDA complex's excited state. The gaussian16 output files were analyzed using Multiwfn 3.8^[5-6] and VMD^[7-8] software to depict the complexes' HOMO and LUMO molecular orbitals in the ground and excited states, as well as the electrostatic potential.

The Quantum Theory of Atoms in Molecules (QTAIM) analysis was done on both the ground and excited states of the EDA complex using Multiwfn3.8. The default settings of the Multiwfn 3.8 software were used to compute the five files required to draw the electrostatic potential map, which were then passed to VMD 1.3.9 for plotting the ESP map.



Figure S10. DFT calculations

For the ground and excited states of the complex, the atomic connections and numbering are shown in Figure S11. The detailed geometric parameters are shown in Figures S12 and S13, respectively.



Figure S11. The plot of ground state and excited state of the EDA complex



Figure S12. The geometric parameters of the ground state and excited state of the complex

7.2 Initial and optimized geometrical parameters of the ground and excited state of the EDA complex

Initial geometrical parameters of ground state of complexes

Ν	-0.92124	1.85191	0.49029
С	0.02449	1.52199	-0.47633
Ν	1.34313	1.58887	-0.05476
Ν	1.73597	2.04619	1.14349
С	0.84819	2.41633	1.99585
С	-0.59368	2.40747	1.72032
0	-1.43528	2.84916	2.48369
0	-0.27959	1.17895	-1.6041
С	-2.33994	1.79751	0.10614
С	2.41588	1.35567	-1.02884
Н	1.18851	2.78626	2.95663
Н	-2.44974	0.95686	-0.57794
Н	-2.8965	1.5833	1.02023

Н	3.27692 1.01937 -0.44805
Н	2.09373 0.54513 -1.68277
С	3.81167 -1.8103 -1.55288
С	5.2131 -1.19444 -1.81873
С	5.54429 -1.30994 -0.30248
С	4.06931 -1.53022 -0.09744
Ν	3.36315 -1.31089 0.93315
0	2.00102 -1.48852 0.57224
С	1.13414 -1.22082 1.57058
0	1.44377 -0.93358 2.69875
С	-0.27332 -1.3002 1.07354
С	-1.27588 -0.82165 1.92107
С	-2.5945 -0.80838 1.49095
С	-2.89934 -1.27702 0.21329
С	-1.90935 -1.77205 -0.63047
С	-0.58754 -1.78434 -0.19783
С	-4.32811 -1.24354 -0.24673
Н	3.78197 -2.88655 -1.74842
Н	2.93749 -1.32422 -1.98793
Н	5.12874 -0.15299 -2.13042
Н	5.8653 -1.74108 -2.49947
Н	6.12108 -2.21057 -0.07378
Н	5.98385 -0.4493 0.2042
Н	-1.00752 -0.44645 2.90244
Н	-3.37871 -0.42037 2.13288
Н	-2.16311 -2.12807 -1.62301
Н	0.19343 -2.1534 -0.85307
С	-2.79336 3.10126 -0.53192
Н	-2.22057 3.30413 -1.44044
Н	-3.85134 3.03494 -0.79824
Н	-2.6634 3.93461 0.1631
С	2.73397 2.61651 -1.81576
Н	3.55629 2.42449 -2.50963
Н	1.86386 2.94067 -2.3926
Н	3.03084 3.42389 -1.1403

F	-4.75635	0.03593	-0.29223
F	-5.09498	-1.94436	0.6154
F	-4.41772	-1.79209	-1.477

The optimized geometric parameters of the ground state of the complex

N,0,-1.2149309644,1.921224904,0.2120955628 C,0,-0.2743109377,1.6514241408,-0.7754264373 N,0,1.0253241597,1.497329064, -0.3271554394 N,0,1.42214026,1.6963456147,0.937629026 C,0,0.5478449999,1.9940786629,1.8270705303 C,0,-0.8822994766,2.154686597,1.5369415304 O,0,-1.7052563986,2.4655927059,2.3748477379 O,0,-0.5692485101,1.5365741478,-1.9472262018 C,0,-2.6130800263,2.1094862536,-0.2054499818 C,0,2.091064072,1.2399371298,-1.3037959041 H,0,0.8879569694,2.1421995416,2.8446064043 H,0,-2.7895363882,1.4404563394,-1.0453252656 H,0,-3.2317581359,1.79677304,0.6342288158 H,0,2.8972545425,0.7729250947,-0.739985917 H,0,1.7063648517,0.5227342545,-2.0281195317 C,0,4.0302309439,-1.9357222626,-1.4010547383 C,0,5.4695294305,-1.422165328,-1.6923149784 C,0,5.7598160218,-1.3987260726,-0.1624166519 C,0,4.2736130942,-1.5352215977,0.0295480722 N,0,3.5608653587,-1.2074576555,1.0234936224 O,0,2.1964853596,-1.3632395765,0.6691815635 C,0,1.3431392478,-1.2574936996,1.707140728 O,0,1.6684418132,-1.1786322453,2.8581420082 C,0,-0.0731223619,-1.2595963698,1.2219507054 C,0,-1.0772500354,-1.0406676937,2.1650732582 C,0,-2.4053360207,-0.9972230723,1.7659549679 C,0,-2.7157982032,-1.1816289757,0.4215115173 C,0,-1.7226005041,-1.4023512358,-0.527118487 C,0,-0.3934502593,-1.4365224749,-0.1250154773 C,0,-4.1553143825,-1.1838809587,-0.0038394733 H,0,3.9485208235,-3.0217156539,-1.4914528052

H,0,3.1891674418,-1.4603119451,-1.9049324432
H,0,5.4581305304,-0.4175149944,-2.1140341465
H,0,6.1019005343,-2.0721659602,-2.2929083336
H,0,6.2827019117,-2.2983382619,0.1693657889
H,0,6.2286148972,-0.5144047571,0.2672068902
H,0,-0.8115577451,-0.8922498098,3.2048728786
H,0,-3.1888393239,-0.8158126341,2.4920074236
H,0,-1.9786594096,-1.5366510604,-1.5710795577
H,0,0.3867921693,-1.5933489559,-0.8595714539
C,0,-2.8894226275,3.5568550206,-0.5831708465
H,0,-2.2655766377,3.8633486122,-1.4250302697
H,0,-3.9365266354,3.6651957587,-0.8730174669
H,0,-2.6949287801,4.221225669,0.2610820771
C,0,2.5609948832,2.5191625762,-1.9766979863
H,0,3.3739514675,2.2915469803,-2.6694920932
H,0,1.7500697957,2.9869107824,-2.5376532811
H,0,2.9310970776,3.2265935508,-1.2308626934
F,0,-4.9110908825,-0.3648556213,0.743357273
F,0,-4.7049983299,-2.4100871784,0.1033353847
F,0,-4.3141111507,-0.8085704997,-1.2818263249

Initial geometric parameters of excited states of complexes

Ν	0	-1.21493	1.92123	0.2121
С	0	-0.27431	1.65143	-0.77542
Ν	0	1.02533	1.49733	-0.32715
Ν	0	1.42214	1.69634	0.93763
С	0	0.54785	1.99407	1.82708
С	0	-0.8823	2.15468	1.53695
0	0	-1.70525	2.46559	2.37485
0	0	-0.56925	1.53658	-1.94722
С	0	-2.61308	2.10949	-0.20545
С	0	2.09107	1.23994	-1.30379
Н	0	0.88796	2.14219	2.84461
Н	0	-2.78953	1.44046	-1.04532
Н	0	-3.23176	1.79678	0.63423
Н	0	2.89726	0.77292	-0.73998
Н	0	1.70637	0.52274	-2.02812
С	0	4.03023	-1.93572	-1.40106
С	0	5.46953	-1.42217	-1.69232

С	0	5.75981 -1.39873 -0.16242
С	0	4.27361 -1.53523 0.02954
Ν	0	3.56086 -1.20747 1.02349
0	0	2.19648 -1.36324 0.66918
С	0	1.34314 -1.2575 1.70714
0	0	1.66844 -1.17864 2.85814
С	0	-0.07312 -1.2596 1.22195
С	0	-1.07725 -1.04067 2.16507
С	0	-2.40534 -0.99722 1.76595
С	0	-2.7158 -1.18163 0.42151
С	0	-1.7226 -1.40235 -0.52712
С	0	-0.39345 -1.43652 -0.12502
С	0	-4.15532 -1.18387 -0.00384
Н	0	3.94852 -3.02172 -1.49146
Н	0	3.18916 -1.46031 -1.90494
Н	0	5.45813 -0.41751 -2.11403
Н	0	6.1019 -2.07216 -2.29292
Н	0	6.2827 -2.29835 0.16936
Н	0	6.22861 -0.51441 0.26721
Н	0	-0.81156 -0.89226 3.20487
Н	0	-3.18884 -0.81581 2.49201
Н	0	-1.97866 -1.53664 -1.57108
Н	0	0.38679 -1.59335 -0.85958
С	0	-2.88942 3.55686 -0.58316
Н	0	-2.26557 3.86336 -1.42502
Н	0	-3.93652 3.6652 -0.87301
Н	0	-2.69492 4.22123 0.26109
С	0	2.561 2.51916 -1.97669
Н	0	3.37396 2.29155 -2.66949
Н	0	1.75007 2.98691 -2.53765
Н	0	2.9311 3.22659 -1.23085
F	0	-4.91109 -0.36485 0.74336
F	0	-4.705 -2.41008 0.10333
F	0	-4.31411 -0.80856 -1.28183

The optimized geometric parameters of the excited state of the complex

N,0,-0.6408516883,1.4622025176,-0.1298506355 C,0,0.351181121,0.8903791508,-0.8708021885 N,0,1.6271713206,1.0529496269,-0.1791141573 N,0,1.5468958014,0.8946506414,1.1161323313 C,0,0.8117033119,1.7952588946,1.8138485735 C,0,-0.4222774232,2.1237391925,1.1446040535 O,0,-1.3045068398,2.8277084079,1.6024874697 O,0,0.2704089147,0.4495740465,-1.9844302086 C,0,-1.9449423299,1.6622317395,-0.7833096474 C,0,2.5183886277,2.0971286726,-0.7521447546 H,0,0.9162369371,1.9067116006,2.8821738242 H,0,-2.1332218266,0.7807135069,-1.3944110793 H,0,-2.6899743076,1.7039967893,0.0099466731 H,0,3.3424690409,2.1885694751,-0.045683134 H,0,2.8980882645,1.67453795,-1.6851598559 C,0,3.4643825228,-1.4427741251,-1.7057095302 C,0,4.8963544617,-0.8760234189,-1.9254510297 C,0,5.3637177278,-1.5768310657,-0.6154020261 C,0,3.9042112378,-1.7729277057,-0.3046184922 N,0,3.3402619409,-1.9639975178,0.8127570615 O,0,1.9375618257,-1.9741640564,0.6093136269 C,0,1.2204600751,-1.7969099027,1.7383701794 O,0,1.6739969762,-1.7623448555,2.8474802912 C,0,-0.2269427714,-1.6240947378,1.4057113049 C,0,-1.0326761604,-1.0047844146,2.3599037042 C,0,-2.3642243051,-0.738271986,2.0742550502 C,0,-2.8802318659,-1.1140210991,0.8378069453 C,0,-2.0901804115,-1.7545667267,-0.1117636644 C,0,-0.7531213715,-2.0009946992,0.1695444492 C,0,-4.3243414391,-0.8509226042,0.5288642902 H,0,3.2839149558,-2.3537866215,-2.282245156 H,0,2.6079404678,-0.775082679,-1.8019165966 H,0,4.9186928301,0.2092613575,-1.8312589864 H.0.5.4006357233.-1.1811767176.-2.8397462619 H,0,5.8552376957,-2.5317491607,-0.8138738604 H,0,5.9438425702,-1.0022685135,0.1057491725 H,0,-0.6068098671,-0.7130406879,3.3121831748 H.0.-2.9893404024,-0.2354479941,2.8022154481 H.0.-2.5076700923,-2.0420145448,-1.0696290092 H,0,-0.1253050606,-2.4776791194,-0.5724574845 C,0,-1.9667078714,2.928633709,-1.6251874633

H,0,-1.2414043189,2.8689087811,-2.4394149557 H,0,-2.9595254428,3.058966029,-2.0613936649 H,0,-1.7407001827,3.8032280029,-1.0118564385 C,0,1.8325055923,3.4346541642,-1.0054938418 H,0,2.5701102836,4.1138717463,-1.4381290374 H,0,1.009245028,3.3383234467,-1.7164403596 H,0,1.461256863,3.875297804,-0.0784689278 F,0,-4.8111646326,0.1996301785,1.2063083038 F,0,-5.1068762889,-1.90273309,0.8452582482 F,0,-4.5308666879,-0.6064694976,-0.7748821478

7.3 QTAIM analysis with multiwfn 3.08

For the ground and excited states of the EDA complex, the BCP paths are shown in Figure S13 and S14, respectively. The QTAIM analysis outcome are listed in table S3-S4.



Figure S13. The BCPs path for ground state of the EDA complex by QTAIM analysis



Figure S14. The BCPs path for excited state of the EDA complex by QTAIM analysis

No . of BCP	conne ct atoms	ρ	∇ ²ρ	λ1	λ2	λ3	V (r)	H (r)	G (r)	eta index	V(r)/G(r)	BE(kc al/mol)
91	F51 H12	0.00 446	0.01 886	0.00213	- 0.00175	0.02 27	- 0.00300	0.00 086	0.003 855	0.09 37	0.777 1	- 0.9398
85	C28 H12	0.00 678	0.02 110	- 0.00416	- 0.00121	0.02 65	- 0.00336	0.00 096	0.004 319	0.15 73	0.778 5	1.0550
80	C29 N1	0.00 640	0.01 950	- 0.00194	- 0.00046	0.02 19	0.00328	0.00 080	0.004 078	0.08 84	0.804 8	1.0298
71	C22 N4	0.01 282	0.04 924	- 0.00768	0.00682	0.06 37	- 0.00893	0.00 169	0.010 622	0.12 04	0.841 0	- 2.8029
98	H32 08	0.00 662	0.02 053	0.00542	0.00374	0.02 97	0.00402	0.00 056	0.004 577	0.18 26	0.878 7	1.2618
94	H32 N3	0.00 905	0.02 587	- 0.00745	0.00695	0.04 03	- 0.00514	0.00 066	0.005 806	0.18 50	0.886 0	- 1.6140
111	H33 H15	0.00 417	0.01 331	0.00317	0.00253	0.01 90	- 0.00224	0.00 054	0.002 784	0.16 67	0.805 3	0.7035
12 1	H42 H47	0.00 527	0.01 598	0.00379	0.00312	0.02 29	- 0.00268	0.00 066	0.003 338	0.16 58	0.803 5	- 0.8416

Table S3. QTAIM analysis of excited state of the EDA complex

Table S4. QTAIM analysis of ground state of the EDA complex

No . of BCP	conne ct atoms	ρ	$\nabla^2 \rho$	λ1	λ2	λ3	V (r)	H(r)	G (r)	eta index	V(r)/G(r)	BE(kc al/mol)
81	F49 H13	0.00 485	0.01 938	- 0.00369	- 0.00295	0.026	- 0.00327	0.000 79	0.004	0.1 417	0.80 57	-
92	F51 H12	0.00 488	0.01 926	0.00379	0.00290	0.025 9	0.00328	0.000 77	0.004 05	0.1 461	0.81 10	1.0303
85	C27 C9	0.00 620	0.02 132	0.00263	0.00066	0.024 6	- 0.00336	0.000 98	0.004 35	0.1 069	0.77 35	- 1.0545
74	C25 C6	0.00 641	0.02 048	- 0.00198	- 0.00040	0.022 9	0.00313	0.001 00	0.004 12	0.0 867	0.75 86	- 0.9815
90	C29 N3	0.00 786	0.02 307	0.00382	0.00174	0.028 6	0.00416	0.000 80	0.004 96	0.1 334	0.83 79	- 1.3046
80	C22 N4	0.00 760	0.02 830	0.00331	0.00164	0.033	0.00453	0.001 27	0.005 80	0.0 996	0.78 10	- 1.4222
95	O21 H14	0.00 755	0.02 723	- 0.00580	0.00391	0.037 0	0.00521	0.000 80	0.006 01	0.1 571	0.86 73	- 1.6357
98	N20 H14	0.00 668	0.02 168	- 0.00388	0.00157	0.027 1	- 0.00385	0.000 79	0.004 63	0.1 429	0.83 00	- 1.2066
10 1	H32 H14	0.00 543	0.01 861	0.00424	0.00100	0.023	0.00294	0.000 86	0.003 79	0.1 777	0.77 39	0.9213

M062X/6-311+G(d,p) computed QTAIM topological parameters at the BCPs(bond critical points) of the Ground and Excited states of the EDA complex . ρ = electron density. $\nabla^2 \rho$ = Laplacian of electron density. λ = eigenvalues of hessian. V(r) potential energy density. H(r) =

energy density. G(r) = Lagrangian kinetic energy. ρ , $\nabla^2 \rho$, V(r), H(r), G(r) are in atomic units. Binding energy (BE) in kcal/mol.

The QTAIM analysis results are listed in table 1 and table 2. The Laplacian of electron densities at the bond critical points (BCPs) of complex are positive, Hessian matrix with two negative and one positive eigenvalues. Based on existing literature ^[9-11], the eta index ^[10-11] and $|V(r)/G(r)|^{[9]}$ at the BCPs in complex are less than 1, and the Binding energies lie between - 0.8 and -3.0 kcal/mol, indicating that these atom pairs in both ground and excited states of the EDA complex exist weak interactions, which can be classified as closed-shell interactions.

8. Characterization Data for Products



4-(2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3aa)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 94% isolated yield (67.7 mg).

¹H NMR (500 MHz, CDCl₃) δ7.50 – 7.46 (m, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.28 (m, 6H), 5.10 (s, 2H), 5.08 (s, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.97 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 155.6, 148.9, 143.4, 135.6, 135.5, 129.5, 128.9, 128.7, 128.5, 128.2, 119.3, 55.3, 44.4, 29.0, 21.9, 16.6.



4-(2,4-Bis(4-methylbenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile (**3ab**)¹³: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 79% isolated yield (61.3 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.39 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 5.05 (s, 2H), 5.04 (s, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.37 (t, J = 7 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 2.05 – 1.97 (m, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.9, 148.9, 143.3, 138.3, 138.0, 132.7, 132.6, 129.6, 129.5, 129.3, 128.9, 119.3, 55.0, 44.1, 28.9, 21.9, 21.3, 16.6. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₂₃H₂₅N₄O₂, 389.1972; Found: 389.1975.



4-(2,4-Bis(4-bromobenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile

 $(3ac)^{12}$: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 86% isolated yield (76.6 mg), m. p. = 108.6 - 110.8 °C.

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 2H), 5.01 (s, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.39 (t, *J* = 7.1 Hz, 2H), 2.05 – 1.97 (m, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.7, 148.8, 143.8, 134.4, 134.3, 132.1, 131.8, 131.4, 130.6, 122.7, 122.4, 119.2, 54.7, 43.8, 29.1, 21.9, 16.7.



4-(2,4-Diallyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3ad)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 78% isolated yield (40.5mg).

¹H NMR (500 MHz, CDCl₃) δ 5.98 – 5.80 (m, 2H), 5.34 – 5.22 (m, 4H), 4.58 – 4.50 (m, 4H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.07-1.99 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 155.7, 148.5, 143.4, 131.5, 130.4, 119.5, 119.3, 119.3, 54.1, 43.1, 29.1, 22.1, 16.8.



4-(2,4-Diethyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3ae):

purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 70% isolated yield (33.0 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 4.04 – 3.94 (m, 4H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 2.08 – 2.00 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ 156.0, 148.5, 143.1, 119.3, 46.9, 36.3, 29.1, 22.1, 16.8, 13.5, 12.6. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₁₁H₁₇N₄O₂, 237.1346; Found: 237.1350.



4-(4-Benzyl-2-ethyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3af)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 88% isolated yield (52.5 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.6 Hz, 2H), 7.34 – 7.28 (m, 3H), 5.09 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.07 – 1.99 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ 156.0, 148.7, 143.2, 135.6, 129.6, 128.7, 128.2, 119.3, 47.0, 44.3, 29.1, 22.1, 16.8, 13.5.



4-(4-Benzyl-3,5-dioxo-2-(pent-4-en-1-yl)-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile (**3ag):** purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 73% isolated yield (49.4 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.28 (m, 3H), 5.84 – 5.74 (m, 1H), 5.09 (s, 2H), 5.06 – 5.00 (m, 1H), 4.98 (d, *J* = 10.2 Hz, 1H)), 3.99 – 3.92 (m, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.15 – 2.07 (m, 2H), 2.07 – 1.99 (m, 2H), 1.88 – 1.80 (m, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 156.0, 148.9, 143.2, 137.2, 135.6, 129.6, 128.7, 128.2, 119.3, 115.6, 51.4, 44.3, 30.7, 29.2, 27.4, 22.1, 16.8. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₁₉H₂₃N₄O₂, 339.1816; Found: 339.1821.



4-(4-Benzyl-3,5-dioxo-2-(2-oxo-2-phenylethyl)-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butane-nitrile (3ah)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 99% isolated yield (76.9 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 6.9 Hz, 1H), 7.51 (t, *J* = 7.1 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.26 (m, 3H), 5.39 (s, 2H), 5.11 (s, 2H), 2.78 (t, *J* = 7.3 Hz, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.97 (m, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 191.8, 156.0, 149.4, 144.0, 135.4, 134.4, 134.3, 129.3, 129.1, 128.7, 128.2, 128.1, 119.3, 57.4, 44.4, 29.0, 21.9, 16.6.



Ethyl 2-(4-benzyl-6-(3-cyanopropyl)-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)acetate- $(3ai)^{12}$: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 94% isolated yield (66.9 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.45 (d, *J* = 6.7 Hz, 2H), 7.34 – 7.27 (m, 3H), 5.09 (s, 2H), 4.67 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.98 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ 167.6, 155.9, 149.1, 144.1, 135.3, 129.4, 128.7, 128.3, 119.3, 62.1, 52.7, 44.4, 29.0, 21.9, 16.6, 14.2.



4-(2-Benzyl-4-(4-methylbenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3aj): purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 92% isolated yield (68.8 mg).

¹**H** NMR (500 MHz, CDCl₃) δ 7.42 – 7.32 (m, 7H), 7.13 (d, J = 7.7 Hz, 2H), 5.09 (s, 2H), 5.05 (s, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.36 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.05 – 1.97 (m, 2H). ¹³**C** NMR (125 MHz, CDCl₃) δ 155.8, 148.9, 143.4, 138.1, 135.7, 132.6, 129.6, 129.3, 128.9, 128.4, 119.3, 55.2, 44.1, 28.9, 21.9, 21.3, 16.6. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₃N₄O₂, 375.1816; Found: 375.1819.



4-(2-Benzyl-4-(4-bromobenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile $(3ak)^{12}$: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 87% isolated yield (76.2 mg), m. p. = 122.6 - 123.8 °C.

¹**H NMR** (500 MHz, CDCl₃) δ 7.43 (d, J = 8.4 Hz, 2H), 7.41 – 7.30 (m, 8H), 5.09 (s, 2H), 5.02 (s, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.36 (t, J = 7.2 Hz, 2H), 2.05 – 1.97 (m, 2H). ¹³**C NMR** (125 MHz,

CDCl₃) δ 155.8, 148.8, 143.4, 135.5, 134.4, 131.8, 131.4, 128.9, 128.6, 128.5, 122.4, 119.2, 55.3, 43.7, 28.9, 21.8, 16.6.



4-(2-Benzyl-4-ethyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3al):

purify-cation by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 82% isolated yield (48.9 mg).

¹**H** NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.4 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.09 (s, 2H), 3.98 (q, J = 7.1 Hz, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.38 (t, J = 7.2 Hz, 2H), 2.06 – 1.98 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). ¹³**C** NMR (125 MHz, CDCl₃) δ 155.8, 148.7, 143.3, 135.8, 128.92, 128.88, 128.4, 119.3, 55.2, 36.4, 29.0, 21.9, 16.6, 12.6. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₁₆H₁₉N₄O₂, 299.1503; Found: 299.1507.



4-(4-Benzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3am)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 94% isolated yield (50.8 mg), m. p. = 114.6 - 115.2 °C.

¹H NMR (500 MHz, CDCl₃) δ 10.56 (s, 1H), 7.47 (d, *J* = 6.4 Hz, 2H), 7.34 – 7.28 (m, 3H), 5.08 (s, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.06 – 1.98 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 156.0, 150.2, 144.5, 135.2, 129.5, 128.7, 128.4, 119.3, 43.8, 29.0, 21.8, 16.8.



4-(4-(4-Methylbenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3an): purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 75% isolated yield (42.6 mg), m. p. = 49 - 50.2 °C.

¹H NMR (500 MHz, CDCl₃) δ 10.17 – 9.94 (m, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.04 (s, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.06 – 1.98 (m, 2H).
¹³C NMR (125 MHz, CDCl₃) δ 156.0, 150.0, 144.5, 138.3, 132.3, 129.6, 129.4, 119.3, 43.6,

29.0, 21.8, 21.3, 16.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}N_4O_2$, 285.1346; Found: 285.1345.



4-(4-(4-Bromobenzyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3ao)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 96% isolated yield (66.8 mg), m. p. = 134.5 - 135.2 °C.

¹**H NMR** (500 MHz, CDCl₃) δ 10.35 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.02 (s, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.06 – 1.98 (m, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.9, 149.9, 144.5, 134.2, 131.9, 131.4, 122.5, 119.3, 43.2, 29.0, 21.8, 16.8.



Bis(2,6-dimethylhept-5-en-1-yl)4,4'-((6-(3-cyanopropyl)-3,5-dioxo-1,2,4-triazine-2,4(3H,-5H)diyl)bis(methylene))dibenzoate(3ap): purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 73% isolated yield (101.7 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 5.13 (s, 2H), 5.11 (s, 2H), 5.08 (t, *J* = 7.1 Hz, 2H), 4.38 – 4.30 (m, 4H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.05 – 1.95 (m, 6H), 1.82 – 1.76 (m, 2H), 1.65 (s, 6H), 1.62 (d, *J* = 6.1 Hz, 2H), 1.59 (s, 6H), 1.42 – 1.35 (m, 2H), 1.26 – 1.20 (m, 2H), 0.96 – 0.94 (2d, *J* = 6.5 Hz, 6H). ¹³**C NMR** (125 MHz, CDCl₃) δ 166.3, 166.2, 155.7, 148.8, 143.9, 140.2, 140.1, 131.4, 130.6, 130.4, 130.1, 130.0, 129.2, 128.6, 124.6, 119.1, 63.74, 63.66, 55.0, 44.1, 37.0, 35.5, 29.6, 29.1, 25.8, 25.5, 21.9, 19.6, 17.7, 16.7. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₄₃H₅₇N₄O₆, 725.4273; Found: 725.4274



2,6-Dimethylhept-5-en-1-yl4-((6-(3-cyanopropyl)-3,5-dioxo-2,5-dihydro-1,2,4-triazin-

4(3H)yl)methyl)benzoate(3aq): purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 68% isolated yield (59.6 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 10.27 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 5.12 (s, 2H), 5.08 (t, J = 7.0 Hz, 1H), 4.38 – 4.29 (m, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 2.05– 1.91 (m, 4H), 1.83 – 1.75 (m, 1H), 1.66 (s, 3H), 1.64 – 1.60 (m, 1H), 1.59 (s, 3H), 1.57 – 1.50 (m, 1H), 1.42 – 1.34 (m, 1H), 1.24 – 1.17 (m, 1H), 0.95 (d, J = 6.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 155.9, 149.9, 144.5, 140.0, 131.5, 130.4, 130.0, 129.2, 124.6, 119.2, 63.8, 43.4, 37.1, 35.5, 29.7, 29.0, 25.8, 25.5, 21.8, 19.6, 17.8, 16.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₅H₃₃N₄O₄, 453.2496; Found: 453.2500.



4-(2-(3,5-Dichloro-4-((4-chlorophenyl)(isocyano)methyl)phenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)butanenitrile(3ar)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 3:1), red solid was obtained with 74% isolated yield (70.0 mg), m. p. = 215.1 - 216.2 °C.

¹H NMR (500 MHz, DMSO-d6) δ 12.53 (s, 1H), 7.85 (s, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 1.95 – 1.87 (m, 2H).
¹³C NMR (125 MHz, DMSO-d6) δ 146.1, 141.8, 134.6, 132.8, 131.9, 129.1, 129.0, 128.5, 125.5, 120.6, 117.0, 36.7, 28.2, 21.5, 15.6.



(1S,2S,4S)-4,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 4-((6-(3-cyanopropyl)-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)methyl)benzoate(3as): purification by flash column chromatography (petroleum ether/ethyl acetate = 3:1), colorless oil was obtained with 95% isolated yield (85.5 mg).

¹**H NMR** (500 MHz, DMSO-d6) δ 10.37 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz,

2H), 5.11 (s, 2H), 4.88 (dd, J = 7.6, 3.8 Hz, 1H), 2.76 (t, J = 7.3 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 2.04 – 1.99 (m, 2H), 1.94 – 1.82 (m, 2H), 1.79 (t, J = 4.0 Hz, 1H), 1.78 – 1.67 (m, 2H), 1.63 – 1.55 (m, 1H), 1.23 – 1.17 (m, 1H), 1.09 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H). ¹³C NMR (125 MHz, DMSO-d6) δ 170.01, 161.44, 154.61, 148.54, 146.70, 134.38, 134.25, 133.09, 86.00, 53.81, 51.86, 49.64, 47.59, 43.56, 38.34, 33.78, 31.81, 26.75, 25.14, 25.03, 20.84, 16.62. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₂₅H₃₁N₄O₄⁺, 451.2340; Found: 451.2324.



2-(6-(3-Cyanopropyl)-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)ethyl 2-(4-isobutylphenyl) propanoate(3at) purification by flash column chromatography (petroleum ether/ethyl acetate = 4:1), colorless oil was obtained with 83% isolated yield (68.4 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 9.98 (s, 1H), 7.15 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.46 – 4.40 (m, 1H), 4.30 – 4.22 (m, 2H), 4.20 – 4.13 (m, 1H), 3.64 (q, J = 7.1 Hz, 1H), 2.74 (t, J =7.3 Hz, 2H), 2.44 (t, J = 7.6 Hz, 4H), 2.07 – 1.98 (m, 2H), 1.88 – 1.78 (m, 1H), 1.45 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H). ¹³**C NMR** (125 MHz, CDCl₃) δ 174.9, 156.0, 149.8, 144.2, 140.8, 137.4, 129.4, 127.3, 119.2, 61.0, 45.1, 45.1, 39.5, 30.3, 29.0, 22.5, 21.8, 18.5, 16.7. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₂₂H₂₉N₄O₄, 413.2183; Found: 413.2180.



2-(6-(3-Cyanopropyl)-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)ethyl 5-(2,5-dimethylp-henyl)2,2-dimethylpentanoate(3au): purification by flash column chromatography (petroleum ether/ethyl acetate = 4:1), colorless oil was obtained with 90% isolated yield (79.2 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 10.35 (s, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 7.4 Hz, 1H), 6.59 (s, 1H), 4.35 (t, J = 5.1 Hz, 2H), 4.22 (t, J = 5.1 Hz, 2H), 3.89 (t, J = 5.6 Hz, 2H), 2.73 (t, J = 7.3 Hz, 2H), 2.39 (t, J = 7.1 Hz, 2H), 2.30 (s, 3H), 2.15 (s, 3H), 2.03 – 1.95 (m, 2H), 1.72 – 1.64 (m, 4H), 1.17 (s, 6H). ¹³**C NMR** (125 MHz, CDCl₃) δ 177.9, 157.0, 156.0, 150.0, 144.3, 136.6, 130.4, 123.6, 120.8, 119.2, 112.0, 68.0, 60.8, 42.2, 39.5, 36.9, 29.0, 25.1, 21.8, 21.5, 16.6, 15.9. **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₂₄H₃₃N₄O₅, 457.2445; Found: 457.2446.



tert-Butyl (1-cyano-3-(2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)propan-2-yl)carbamate(3ba)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 93% isolated yield (88.4 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.46 (d, *J* = 7.1 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.27 (m, 6H), 5.16 (d, *J* = 7.8 Hz, 1H), 5.12 – 5.04 (m, 4H), 4.27 – 4.19 (m, 1H), 2.91 (d, *J* = 5.8 Hz, 2H), 2.76 (dd, *J* = 16.8, 5.5 Hz, 1H), 2.61 (dd, *J* = 16.8, 4.3 Hz, 1H), 1.39 (s, 9H). ¹³**C NMR** (125 MHz, CDCl₃) δ 156.4, 155.0, 148.7, 141.3, 135.4, 135.3, 129.4, 128.93, 128.86, 128.7, 128.5, 128.2, 117.1, 80.4, 55.5, 45.7, 44.5, 34.4, 28.3, 23.4.



4-(2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)-3-phenylbutanenitrile(3ca)³: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 90% isolated yield (78.5 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.42 – 7.38 (m, 2H), 7.33 – 7.30 (m, 4H), 7.30 – 7.24 (m, 5H), 7.21 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.18 (dd, *J* = 7.6, 1.9 Hz, 2H), 5.04 (d, *J* = 6.5 Hz, 2H), 5.01 (d, *J* = 6.2 Hz, 2H), 3.61 – 3.54 (m, 1H), 3.15 – 3.05 (m, 2H), 2.69 – 2.59 (m, 2H). ¹³**C NMR** (125 MHz, CDCl3) δ 155.9, 148.7, 142.4, 140.3, 135.6, 135.4, 129.3, 129.0, 128.8, 128.7, 128.6, 128.3, 128.2, 127.8, 127.3, 118.2, 55.3, 44.3, 39.0, 35.3, 24.6.



Ethyl 3-cyano-2-((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methyl)propanoate(3da)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 91% isolated yield (78.6 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.47 (d, J = 6.9 Hz, 2H), 7.39 – 7.28 (m, 8H), 5.12 – 5.01 (m, 4H), 4.14 – 4.06 (m, 1H), 4.06 – 3.98 (m, 1H), 3.26 – 3.19 (m, 1H), 3.12 (dd, J = 16.4, 7.1 Hz, 1H), 2.96 (dd, J = 16.4, 6.6 Hz, 1H), 2.68 (dd, J = 17.0, 6.7 Hz, 1H), 2.59 (dd, J = 17.0, 6.8 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ 171.3, 155.7, 148.8, 141.7, 135.5, 135.4, 129.5, 128.9, 128.8, 128.7, 128.5, 128.3, 117.5, 61.8, 55.3, 44.4, 38.5, 31.3, 19.1, 14.1.



tert-Butyl 3-cyano-2-((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methyl)propanoate(3ea)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 83% isolated yield (76.4 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.7 Hz, 2H), 7.41 – 7.28 (m, 8H), 5.12 – 5.05 (m, 4H), 3.20-3.12 (m, 1H), 3.08 (dd, *J* = 16.2, 7.2 Hz, 1H), 2.89 (dd, *J* = 16.2, 6.7 Hz, 1H), 2.62 (dd, *J* = 16.6, 6.4 Hz, 1H), 2.55 (dd, *J* = 16.9, 6.4 Hz, 1H), 1.37 (s, 9H). ¹³**C NMR** (125 MHz, CDCl₃) δ 170.4, 155.8, 148.9, 142.1, 135.5, 135.4, 129.6, 128.93, 128.87, 128.7, 128.5, 128.3, 117.6, 82.6, 55.3, 44.5, 39.2, 31.4, 27.9, 19.3.



2-((2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methyl)succinonitrile(3fa)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), white solid was obtained with 95% isolated yield (73.2 mg), m. p. = 119.6 - 122.9 °C.

¹**H NMR** (500 MHz, CDCl₃) δ 7.46 (d, J = 6.5 Hz, 2H), 7.42 (d, J = 6.7 Hz, 2H), 7.39 – 7.27 (m, 6H), 5.13 (s, 2H), 5.08 (s, 2H), 3.46 – 3.38 (m, 1H), 3.10 (dd, J = 16.4, 8.3 Hz, 1H), 3.02 (dd, J = 16.4, 6.1 Hz, 1H), 2.72 (d, J = 6.6 Hz, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.6, 148.6, 139.3, 135.10, 135.09, 129.5, 129.03, 128.99, 128.8, 128.7, 128.4, 118.1, 115.3, 55.6, 44.6, 31.8, 25.3, 20.7.



tert-Butyl 3-(cyanomethyl)-3-((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6yl)m-ethyl)azetidine-1-carboxylate(3ga)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 79% isolated yield (79.2 mg).

¹H NMR (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.6 Hz, 2H), 7.40 – 7.27 (m, 8H), 5.09 (s, 2H), 5.07 (s, 2H), 3.81 (d, *J* = 9.2 Hz, 2H), 3.71 (d, *J* = 9.2 Hz, 2H), 3.04 (s, 2H), 2.59 (s, 2H), 1.44 (s, 9H).
¹³C NMR (125 MHz, CDCl₃) δ 156.1, 156.0, 148.7, 141.0, 135.3, 130.5, 129.6, 129.1, 128.74, 128.68, 128.4, 117.1, 80.3, 55.1, 44.6, 35.8, 34.2, 28.4, 25.5.



tert-Butyl 4-(cyanomethyl)-4-((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6yl)m-ethyl)piperidine-1-carboxylate(3ha)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 69% isolated yield (73.0 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.46 (d, *J* = 6.7 Hz, 2H), 7.40 – 7.28 (m, 8H), 5.11 (s, 2H), 5.09(s, 2H), 3.48 – 3.35 (m, 4H), 2.81 (s, 2H), 2.30 (s, 2H), 1.52 – 1.42 (m, 13H). ¹³**C NMR** (125 MHz, CDCl₃) δ 156.5, 154.7, 148.7, 141.8, 135.5, 135.4, 129.5, 129.1, 128.9, 128.7, 128.6, 128.3, 117.6, 80.0, 55.2, 44.7, 35.8, 35.0, 34.2, 28.5, 26.6.



2-((2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methoxy)acetonitrile(3ia)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 79% isolated yield (57.2 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.4 Hz, 2H), 7.41 (d, *J* = 6.4 Hz, 2H), 7.39 – 7.27 (m, 6H), 5.13 (s, 2H), 5.08 (s, 2H), 4.56 (s, 2H), 4.34 (s, 2H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.5, 148.8, 139.6, 135.23, 135.19, 129.6, 128.93, 128.89, 128.7, 128.6, 128.4, 115.8, 67.8, 56.4, 55.7, 44.5.



tert-Butyl (cyanomethyl)((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methyl)carbamate(3ja)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 96% isolated yield (88.5 mg).

¹**H** NMR (500 MHz, CDCl₃) δ 7.48 (s, 2H), 7.42 – 7.27(m, 8H), 5.11 (s, 2H), 5.07 (d, *J* = 15.3 Hz, 2H), 4.45 (d, *J* = 14.8 Hz, 2H), 4.25 (s, 1H), 4.12 (s, 1H), 1.52 (s, 4.5H), 1.37 (s, 4.5H). ¹³**C** NMR (125 MHz, CDCl₃) δ 155.54, 155.51, 154.4, 153.8, 148.8, 139.7, 139.4, 135.43, 135.36, 135.3, 129.6, 128.9, 128.8, 128.7, 128.5, 128.41, 128.35, 128.3, 116.1, 82.7, 82.3, 55.6, 55.5, 47.2, 46.7, 44.4, 44.3, 37.1, 36.1, 28.23, 28.15.



Benzyl (cyanomethyl)((2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)methyl)carbamatee(3ka)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 82% isolated yield (81.2 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.27 (m, 12H), 7.21 (d, *J* = 6.9 Hz, 1H), 5.22 (s, 1H), 5.07 (s, 2H), 5.05 (s, 2H), 4.97 (s, 1H), 4.53 (s, 1H), 4.49 (s, 1H), 4.31 (s, 1H), 4.19 (s, 1H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.5, 155.4, 154.7, 148.74, 148.66, 139.0, 138.9, 135.5, 135.32, 135.29, 135.2, 129.6 129.1 129.0, 128.9, 128.8, 128.74, 128.66, 128.62, 128.55, 128.5, 128.4, 128.2, 115.7, 68.7, 68.5, 55.5, 55.3, 47.6, 46.9, 44.4, 36.8, 36.6.



5-(2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)-5-methylhexanenitrile(3la)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 78% isolated yield (62.7 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.46 (d, *J* = 6.8 Hz, 2H), 7.42 – 7.39 (m, 2H), 7.39 – 7.28 (m, 6H), 5.09 (s, 2H), 5.08 (s, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.93 – 1.87 (m, 2H), 1.47 – 1.38 (m, 2H), 1.31 (s, 6H). ¹³**C NMR** (125 MHz, CDCl₃) δ 154.8, 148.9, 148.6, 135.8, 135.7, 129.3, 128.9, 128.8, 128.7, 128.4, 128.1, 119.6, 55.3, 44.1, 40.2, 38.8, 25.9, 21.2, 17.6.



3-(1-(2,4-Dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)ethoxy)propanenitrile-(**3ma**)¹²: purification by flash column chromatography (petroleum ether/ethyl acetate = 5:1), colorless oil was obtained with 55% isolated yield (42.9 mg).

¹**H NMR** (500 MHz, CDCl₃) δ 7.48 (d, *J* = 6.9 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.29 (m, 6H), 5.18 – 5.06 (m, 4H), 4.70 (q, *J* = 6.5 Hz, 1H), 3.73 – 3.67 (m, 2H), 2.58 – 2.53 (m, 2H), 1.48 (d, *J* = 6.6 Hz, 3H). ¹³**C NMR** (125 MHz, CDCl₃) δ 155.5, 148.8, 143.3, 135.52, 135.46, 129.6, 129.0, 128.9, 128.7, 128.5, 128.3, 117.8, 72.6, 64.6, 55.5, 44.4, 19.1, 18.0.

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10. NMR Spectra of Products

¹H NMR



























































































