Organophotocatalytic Trifluoromethylation of 6-Azauracils

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1. General Information:

All reagents were purchased from commercial sources and used without further purification. 1H NMR spectra were determined on 400 MHz spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants (J) were given in Hz. ¹³C{1H} NMR spectra were recorded at 100 MHz in CDCl₃ solution. ¹⁹F NMR spectra were recorded at 376 MHz in CDCl₃ solution. Chemical shifts as internal standard is referenced to CDCl₃ (δ = 7.26 for ¹H and δ = 77.16 for ¹³C{1H} NMR) for as internal standard. Thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 aluminum sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on silica gel (60-120 mesh or 100–200 mesh). All 6-azouracils¹ were prepared by the reported methods. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. Melting points (M.p.) were determined after recrystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3).

2. Light Information: Kessil 34 W blue LED (Model No. H150-BLUE) was used as a light source for light promoted reactions. Rating of LED: 24VDC 1.5A 34W. Model: H150-BLUE. Range of wavelength: 450-530 nm. Manufacturer: Kessil, 1689 Regatta blvd, Richmond, CA 94804 (www.kessil.com).

3. Reaction Setup: The Borosilicate glass tube was used to carry out light-promoted reaction. The reaction tube was kept 7 cm apart from the exposed of Kessil 34 W blue LED. Regular fan was used to keep up the temperature 28 to 30 °C during the reaction. We did not use any filter.

4. Starting Material Preparation:

4.1. General Procedure for the Synthesis of Azauracils:¹



Alkyl halides (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*-4-alkyl-6-azauracils.

Alkyl halides (2.0 mmol, 1.0 equiv) was added dropwise to a stirring solution of *N*-4- alkyl-6azauracils (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 *N*-2,*N*-4-dialkyl-6azauracils.



The following Azauracils were prepared using the aforesaid literature procedure:

5. Gram-Scale Preparations:

5.1. Synthesis of 3a on 5.0 mmol Scale:



A mixture of 2,4-dibenzyl-1,2,4-triazine-3,5(2H,4H)-dione (1a) (4 mmol, 1.1 g), Langlois' reagent (CF₃SO₂Na) (2) (2.0 equiv., 1.2 g) and 4CzIPN (3 mol%, 94.6 mg) was taken in an oven dried reaction tube. Then DMSO (18 mL) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under open air atmosphere for 24 h. The progress of the reaction was monitored by TLC, and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure product **3a** (844.7 mg, 72%) as a white solid.

6. Radical Trapping Experiment:

A mixture of 2,4-dibenzyl-1,2,4-triazine-3,5(2H,4H)-dione (1a) (0.3 mmol, 88.1 mg), Langlois' reagent (CF₃SO₂Na) (2) (2.0 equiv., 93.6 mg), 4CzIPN (3 mol%, 7.0 mg) and DPE (3.0 equiv., 135.1 mg) was taken in an oven dried reaction tube. Then DMSO (2 mL) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under open air atmosphere for 24 h. After that, the reaction mixture was run for HRMS analysis showed that HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₅H₁₂F₃]⁺: 249.0886; found: 249.0868, we confirmed that DPE trapped radical adduct was found.



HRMS spectra of DPE adduct

7. Fluorescence quenching studies:²

1.0 x 10⁻⁴ M 4CzIPN solution was prepared in DMSO for Photoluminescence studies where as other substrates like a) sodium trifluoromethanesulfinate (CF₃SO₂Na) (**2**), b) 2,4-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (6-azouracil) (**1a**), in DMSO have been made maintaining 1.0 x 10⁻² M concentration.



Fig (S1): Change in Fluorescence intensity of 4CzIPN (1.0 x 10^{-4} M in DMSO) upon incremental addition of a) sodium trifluoromethanesulfinate (CF₃SO₂Na) (**2**), b) 2,4-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (6-azouracil) (**1a**). Excitation wavelength = 360 nm. The quenching phenomena of the photocatalyst in presence of different substrates are explained by the Stern-Volmer plot with the help equation (i).

$$(I_0/I) = K_{SV} [Q] + 1$$
 -----(i)

Here, I_0 and I represent the fluorescence intensity of 4CzIPN in absence and presence of the quencher respectively, K_{SV} is Stern-Volmer quenching constant and [Q] is the concentration of the quencher. If the I_0/I versus [Q] plot are linear, K_{SV} can be estimated accurately. In case

of sodium trifluoromethanesulfinate K_{SV} value obtained from Stern volmer plot is 5.93 x 10³ M⁻¹. It has been observed that the emission intensity of 4CzIPN, which is largely quenched by the gradual addition of sodium trifluoromethanesulfinate (CF₃SO₂Na) (**2**), is moderately affected by the **1a**.



Fig (S2): Stern-Volmer plot from the steady state fluorescence emission of 4CzIPN in presence of quencher in DMSO at 300 K obtained from Fig. (S1).

8. Characterization data of the synthesized compounds (1a-3x):



2,4-dibenzyl-1,2,4-triazine-3,5(2H,4H)-dione (1a): ¹H NMR (CDCI3, 400 MHz): δ 7.49-7.46 (m, 2H), 7.41 (s, 1H), 7.38-7.36 (m, 2H), 7.35-7.27 (m, 3H), 5.10 (s, 2H), 5.07 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.0, 148.8, 135.52, 135.50, 134.6, 129.5, 128.9, 128.8, 128.7, 128.5, 128.2, 55.5, 44.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₇H₁₆N₃O₂]⁺: 294.1237; found: 294.1254.



4-benzyl-2-(2-oxo-2-phenylethyl)-1,2,4-triazine-3,5(2H,4H)-dione (1b): ¹H NMR (CDCl3, 400 MHz): δ 7.97- 7.95 (m, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.34-7.28 (m, 3H), 5.39 (s, 2H), 5.11 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 191.5, 156.0, 149.2, 135.3, 135.2, 135.1, 134.4, 129.3, 129.1, 128.7, 128.2, 128.1, 57.6, 44.1; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₈H₁₆N₃O₃]⁺: 322.1186; found: 322.1208.



Ethyl 2-(4-benzyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)acetate (1c): ¹H NMR (CDCl3, 400 MHz): δ 7.46- 7.42 (m, 3H), 7.34-7.28 (m, 3H), 5.09 (s, 2H), 4.67 (s, 2H), 4.26-4.21 (m, 2H), 1.27 (t, J = 7.6 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.3, 155.8, 148.8, 135.2, 135.0, 129.2, 128.6, 128.2, 62.0, 52.8, 44.0, 14.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₄H₁₆N₃O₄]⁺: 290.1135; found: 290.1154.



4-benzyl-2-butyl-1,2,4-triazine-3,5(2H,4H)-dione (1d): ¹H NMR (CDCl3, 400 MHz): δ 7.42-7.40 (m, 2H), 7.32 (s, 1H), 7.25-7.19 (m, 2H), 5.00 (s, 2H), 3.88 (t, J = 8.4 Hz, 2H), 1.68-1.60 (m, 2H), 1.33-1.24 (m, 2H), 0.87 (t, J = 7.6 Hz, 2H); ${}^{13}C{}^{1H}$ NMR (100 MHz, CDCl₃): δ 156.0, 148.6, 135.5, 134.0, 129.4, 128.5, 128.1, 51.7, 43.8, 30.2, 19.6, 13.6; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₄H₁₈N₃O₂]⁺: 260.1394; found: 260.1402.



4-benzyl-2-methyl-1,2,4-triazine-3,5(2H,4H)-dione (1e): ¹H NMR (CDCl3, 400 MHz): δ 7.42-7.40 (m, 2H), 7.32 (s, 1H), 7.25-7.19 (m, 3H), 5.00 (s, 2H), 3.88 (t, J = 7.6 Hz, 2H), 1.68-1.60 (m, 2H), 1.33-1.24 (m, 2H), 0.87 (t, J = 7.6 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.2, 148.9, 135.5, 134.1, 129.5, 128.7, 128.2, 43.9, 39.7; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₁H₁₂N₃O₂]⁺: 218.0924; found: 218.0902.



2,4-bis(4-methylbenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1f): ¹H NMR (CDCl3, 400 MHz): δ 7.38 (d, J = 6.4 Hz, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.17- 7.12 (m, 4H), 5.06 (s, 2H), 5.03 (s, 2H), 2.34 (s, 3H), 2.33 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.0, 148.7, 138.3, 138.0, 134.5, 132.56, 132.54, 129.5, 129.3, 128.8, 55.2, 43.8, 21.3; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₉H₂₀N₃O₂]⁺: 322.1550; found: 322.1572.



4-(4-methylbenzyl)-2-(4-nitrobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1g): ¹H NMR (CDCl3, 400 MHz): δ 8.20 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.42 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 5.16 (s, 2H), 5.02 (s, 2H), 2.31 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 148.7, 148.0, 142.4, 138.2, 135.2, 132.2, 129.6, 129.5, 129.4, 124.1, 54.7, 43.9, 21.2; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₈H₁₇N₄O₄]⁺: 353.1244; found: 353.1228.



Ethyl 2-(4-(4-methylbenzyl)-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)acetate (1h): ¹H NMR (CDCl3, 400 MHz): δ 7.41 (s, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.04 (s, 2H), 4.66 (s, 2H), 4.26-4.21 (m, 2H), 2.31 (s, 3H), 1.27 (t, J = 7.2 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.3, 155.8, 148.8, 138.0, 135.0, 132.2, 129.3, 129.3, 62.0, 52.8, 43.8, 21.2, 14.1; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₅H₁₈N₃O₄]⁺: 304.1292; found: 304.1309.



2-*isobutyl-4*-(4-*methylbenzyl)*-1,2,4-*triazine*-3,5(2H,4H)-*dione* (1i): ¹H NMR (CDCl3, 400 MHz): δ 7.37 (d, J = 6.4 Hz, 3H), 7.12 (d, J = 7.4 Hz, 2H), 5.05 (s, 2H), 3.77 (d, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.19-2.12 (m, 1H), 0.94 (d, J = 8.0 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.9, 148.9, 137.9, 134.0, 132.6, 129.4, 129.2, 58.8, 43.6, 27.7, 21.2, 19.8; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₅H₂₀N₃O₂]⁺: 274.1550; found: 274.1563.



2,4-bis(4-nitrobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1j): ¹H NMR (CDCl3, 400 MHz): δ 8.17 (d, J = 8.8 Hz, 2H), 8.12 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.47 (s, 1H), 5.18 (s, 2H), 5.13 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.5, 148.6, 148.0, 147.8, 142.1, 142.0, 135.0, 130.3, 129.6, 124.1, 129.6, 124.1, 123.9, 54.8, 43.4; HRMS (ESI-TOF) m/z: [M + Na]⁺ Calcd for [C₁₇H₁₃N₅O₆]⁺: 406.0758; found: 406.0752.



2-(4-bromobenzyl)-4-(4-nitrobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1k): ¹H NMR (CDCl3, 400 MHz): δ 8.19 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.51-7.49 (m, 2H), 7.47 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 5.15(s, 2H), 5.07 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.6, 148.6, 148.0, 142.2, 135.1, 134.1, 131.9, 131.3, 129.6, 124.1, 122.5, 54.7, 43.5; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₁₇H₁₃BrN₄O₄]⁺: 439.0012; found: 439.0032.



2-(2-bromobenzyl)-4-(4-nitrobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1l): ¹H NMR (CDCl3, 400 MHz): δ 8.18 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.46 (s, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.21- 7.18 (m, 2H), 5.26 (s, 2H), 5.18 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 148.8, 138.0, 134.8, 134.7, 133.1, 132.4, 129.7, 129.6, 129.4, 129.3, 127.6, 123.4, 54.8, 43.8, 21.2; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₇H₁₄BrN₄O₄]⁺: 417.0193; found: 417.0172.



2-(3,5-dimethylbenzyl)-4-(4-nitrobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1m): ¹H NMR (CDCl3, 400 MHz): δ 8.16 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.45 (s, 1H), 6.69 (d, J = 5.6 Hz, 1H), 5.14 (s, 2H), 5.03 (s, 2H), 2.29 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 148.4, 147.6, 142.3, 138.4, 135.0, 134.3, 130.1, 130.0, 126.3, 123.7, 55.4, 43.1, 21.2; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₉H₁₉N₄O₄]⁺: 367.1401; found: 367.1385.



2,4-bis(4-bromobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1n): ¹H NMR (CDCl3, 400 MHz): δ 7.48 (d, J = 5.6 Hz, 2H), 7.45 (d, J = 2.4 Hz, 2H), 7.40 (s, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.27-7.24 (m, 2H), 5.02 (s, 2H), 4.99 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.7, 148.6, 134.7, 134.2, 132.07, 132.05, 131.8, 131.3, 130.6, 122.7, 122.5, 54.9, 43.4; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₇H₁₄Br₂N₃O₂]⁺: 449.9447; found: 449.9445.



4-(4-bromobenzyl)-2-(3,3-dimethyl-2-oxobutyl)-1,2,4-triazine-3,5(2H,4H)-dione (10): ¹H NMR (CDCl3, 400 MHz): δ 7.44-7.40 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 5.01 (s, 2H), 4.89 (s, 2H), 1.24 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 207.4, 155.9, 148.9, 134.9, 134.3, 131.8, 131.0, 122.3, 56.1, 43.4, 43.3, 26.2; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₆H₁₉BrN₃O₃]⁺: 380.0604; found: 380.0584.



2,4-bis(2-oxo-2-phenylethyl)-1,2,4-triazine-3,5(2H,4H)-dione (1p): ¹H NMR (CDCl3, 400 MHz): δ 7.89 (t, J = 7.2 Hz, 2H), 7.66-7.61 (m, 2H), 7.55-7.49 (m, 5H), 5.44 (s, 2H), 5.39 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 191.5, 190.2, 155.7, 148.9, 134.9, 134.5, 134.4, 134.3, 134.2, 129.1, 129.0, 128.3, 128.2, 57.6, 46.4; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₉H₁₆N₃O₄]⁺: 350.1135; found: 350.1143.



2,4-diethyl-1,2,4-triazine-3,5(2H,4H)-dione (1q): ¹H NMR (CDCl3, 400 MHz): δ 7.99 (s, 1H), 4.01- 3.96 (m, 2H), 4.95-4.91 (m, 2H), 1.29 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.9, 148.2, 134.1, 46.9, 35.8, 13.3, 12.4; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₇H₁₂N₃O₂]⁺: 170.0924; found: 170.0905.



2,4-dibutyl-1,2,4-triazine-3,5(2H,4H)-dione (1r): ¹H NMR (CDCl3, 400 MHz): δ 7.34 (s, 1H), 3.94 (t, *J* = 7.4 Hz, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 1.74-1.66 (m, 2H), 1.63-1.56 (m, 2H), 1.39-1.30 (m, 4H), 0.95-0.90 (m, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.1, 148.6, 134.0, 51.6, 40.6, 30.2, 29.3, 20.1, 19.7, 13.73, 13.70; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₁H₂₀N₃O₂]⁺: 226.1550; found: 226.1529.



4-benzyl-1,2,4-triazine-3,5(2H,4H)-dione (1s): ¹H NMR (CDCl3, 400 MHz): δ 7.48- 7.46 (m, 2H), 7.41 (s, 1H), 7.34-7.27 (m, 3H), 5.06 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ

156.0, 149.7, 135.6, 135.1, 129.4, 128.7, 128.3, 43.4; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₀H₁₀N₃O₂]⁺: 204.0768; found: 204.0757.



4-(4-methylbenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1t): ¹H NMR (CDCl3, 400 MHz): δ 10.10 (s, 1H), 7.38 (t, J = 8.0 Hz, 3H), 7.12 (d, J = 7.2 Hz, 2H), 5.02 (s, 2H), 2.31 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 156.0, 149.6, 138.2, 135.7, 132.2, 129.5, 129.4, 43.2, 21.2; HRMS (ESI-TOF) m/z: [M + H]⁺ Calcd for [C₁₁H₁₂N₃O₂]⁺: 218.0924; found: 218.0907.



4-(4-bromobenzyl)-1,2,4-triazine-3,5(2H,4H)-dione (1u): ¹H NMR (CDCl3, 400 MHz): δ 9.87 (s, 1H), 7.45- 7.41 (m, 3H), 7.37-7.35 (m, 2H), 5.00 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 155.8, 149.5, 135.6, 134.1, 131.9, 131.3, 122.6, 42.8; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₀H₉BrN₃O₂]⁺: 281.9873; found: 281.9853.



3-(4-(4-nitrobenzyl)-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)propyl 5-(2,5 dimethylphenoxy)-2,2-dimethylpentanoate (**1v**): ¹H NMR (CDCl3, 400 MHz): δ 8.13 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.41 (s, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.64 (d, J = 7.2 Hz, 1H), 6.59 (s, 1H), 5.12 (s, 1H), 4.12- 4.05 (m, 4H), 3.91 (d, J = 5.6 Hz, 2H), 2.29 (s, 3H), 2.15 (s, 3H), 2.12-2.06 (m, 2H), 1.71 (d, J = 2.4 Hz, 4H), 1.22 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 177.6, 156.9, 155.7, 148.4, 147.7, 142.3, 136.5, 134.3, 130.3, 130.2, 123.8, 123.5, 120.8, 111.9, 67.9, 61.1, 48.9, 43.2, 42.2, 37.1, 27.4, 25.25, 25.21, 21.4, 15.8; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₂₈H₃₅N₄O₇]⁺: 539.2500; found: 539.2505.



3-(4-benzyl-3,5-dioxo-4,5-dihydro-1,2,4-triazin-2(3H)-yl)propyl

2-(4

isobutylphenyl)propanoate (1w): ¹H NMR (CDCl3, 400 MHz): δ 7.49- 7.46 (m, 2H), 7.34-7.28 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.06 (s, 2H), 4.12 (t, J = 6.4 Hz, 2H), 3.94 (t, J = 4.4 Hz, 2H), 3.67-3.62 (m, 1H), 2.44 (d, J = 7.2 Hz, 2H), 2.07-2.00 (m, 2H), 1.87-1.81 (m, 1H), 1.47 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 6.8 Hz, 6H); ¹³C{¹H} NMR (100

MHz, CDCl₃): δ 174.6, 155.9, 148.6, 140.6, 137.6, 135.4, 134.3, 129.5, 129.4, 128.7, 128.2, 127.2, 61.7, 49.0, 45.14, 45.12, 44.0, 30.2, 27.3, 22.4, 18.5; HRMS (ESI-TOF) *m*/*z*: [M + H]⁺ Calcd for [C₂₆H₃₂N₃O₄]⁺: 450.2387; found: 450.2381.



3-(3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3H)-yl)propyl 2-(4-isobutylphenyl)propanoate (1x): ¹H NMR (CDCl3, 400 MHz): δ 10.29 (s, 1H), 7.36 (s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 4.15- 4.06 (m, 2H), 3.97- 3.90 (m, 2H), 3.27-3.66 (m, 1H), 2.43 (d, J = 8.2 Hz, 2H), 2.01-1.94 (m, 2H), 1.86-1.79 (m, 2H), 1.48 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 6.8 Hz, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 174.8, 156.0, 149.7, 140.4, 137.4, 135.2, 129.2, 127.1, 62.1, 45.0, 44.9, 37.2, 30.0, 26.4, 22.3, 18.3; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₉H₂₆N₃O₄]⁺: 360.1918; found: 360.1925.

9. References:

(1) (a) Huang, P.-J.; Lee, K.-H. Synthesis and antibacterial evaluation of 6-azapyrimidines with a-methylene-- (4-substituted phenyl) --butyrolactone pharmacophores. *Med. Chem. Res.* **2010**, *20*, 1081. (b) Hwang, L. C.; Yang, S. Y.; Chuang, C. L.; Lee, G. H.; An Optimized Synthesis, Molecular Structure and Characterization of Benzylic Derivatives of 1,2,4-Triazin-3,5(2H,4H)-dione. *Molecules*. **2017**, *22*, 1924.

(2) (a) Cabrera-Afonso, M. J.; Sookezian, A.; Badir, S. O.; Khatib, M. E.; Molander, G. A. Photoinduced 1,2-dicarbofunctionalization of alkenes with organotrifluoroborate nucleophiles *via* radical/polar crossover. *Chem. Sci.* **2021**, *12*, 9189. (b) Sookezian, A.; Molander, G. A. Photoinduced Vicinal 1,2-Difunctionalization of Olefins for the Synthesis of Alkyl Sulfonamides. *Org. Lett.* **2023**, *25*, 1014.

10. NMR spectra [¹H, ¹³C{1H} and ¹⁹F] of synthesized products:
























































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k.

























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S109

















-100 -120 -140 -160 -180 ppm























S128













