Copper-catalyzed [4 + 2] annulation reaction of β-enaminones and aryldiazonium salts without external oxidant: access to highly functionalized 3H-1,2,4-triazines via homogeneous or heterogeneous strategy.

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Experimental procedures and analytical data

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1. General considerations

$^1$H and $^{13}$C{${^1}$H} NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm, CDCl$_3$ ($\delta(^1$H), 7.26 ppm; $\delta(^{13}$C), 77.16 ppm). The HRMS (EI) analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. Analytical TLC plates, Sigma-Aldrich silica gel 60F200 were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. The valence states of elements in the copper catalyst were determined by X-ray photoelectron spectroscopy (XPS) using Thermo K-Alpha XPS. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds 1a-1c, 1e, 1k, 1m, 1n, 2a-2j are known and their spectroscopic feature is in good agreement with that reported in the literature.

2. Supplementary Reference


3. Experimental procedures

3.1 Pathway for the synthesis of pyrazole products
According to the formation of intermediate 5 for the 3H-1,2,4-triazine synthesis, the intermediate A could be formed (Scheme S1). Such imine A could be transformed to secondary amine B with conjugated structure through 1,3-H migration. Finally under the promotion of K₃PO₄, the C-N bond could be formed and the pyrazole product 4a was formed.

![Scheme S1 Pathway for the synthesis of pyrazole products](image)

**3.2 Preparation of β-enaminones 1**

**A typical procedure for the synthesis of β-enaminones (1a-1n) – Synthesis of 1a:** A mixture of 1-phenyl-1,3-butanedione sm1a (324 mg, 2 mmol) and benzylamine (437 μL, 4 mmol) in EtOH (10 mL) were stirred at 80 °C overnight. After 1-phenyl-1,3-butanedione sm1a was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 30:1, v/v), affording 1a (427 mg, 85%) as a yellow solid.

**3.3 Preparation of diazonium salts 2**

\[
\text{NH}_2 + \text{NaNO}_2 + \text{HBF}_4 \rightarrow \text{H}_2\text{O}, 0 \degree \text{C} \rightarrow \text{N}_2\text{BF}_4
\]
A typical procedure for the synthesis of diazonium salts (2a-2j) – Synthesis of 2a: The diazonium salt 2a was prepared according to literature procedure.\textsuperscript{5} Appropriate aniline (25 mmol) was dissolved in water (10 mL) and hydrofluoroboric acid (48% w/w in water, 10.5 mL, 2.0 equiv). After the reaction mixture was cooled to 0 °C, sodium nitrile solution (1.73 g, 25 mmol in 6 mL water) was added dropwise. The reaction mixture was stirred at 0 °C for 40 min. The resulting precipitate was collected by filtration. The crude product was dissolved into acetone, and the solution was gently heated, then diethyl ether was added until the recrystallized product precipitated completely. The diazonium salt 2a (white solid, 3.70 g, 77%) was collected by filtration, washed several times by cold diethyl ether and dried under vacuum.

3.4 Typical procedures for the synthesis of 3H-1,2,4-triazine (3)

A typical procedure for the synthesis of 3H-1,2,4-triazine (3) – Synthesis of 3a: a mixture of β-enaminone 1a (126 mg, 0.5 mmol), diazonium salt 2a (144 mg, 0.75 mmol), CuBr (14 mg, 0.1 mmol), and K\textsubscript{3}PO\textsubscript{4} (212 mg, 1.0 mmol) in 5 mL DMF was stirred at 80 °C for 1.0 h. The reaction mixture was cooled to ambient temperature, filtered through a short pad of celite, rinsed with 20 mL of ethyl acetate, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 15:1, v/v), affording 3a as a yellow liquid (135 mg, 76%).

3.5 Preparation of polyhedron Cu\textsubscript{2}O

0.159 g of Cu(OAc)\textsubscript{2}·H\textsubscript{2}O was dissolved in 40 mL of deionized water in a beaker and stirred with a magnetic stirrer to give a clear solution. 8.0 mL of N\textsubscript{2}H\textsubscript{4}·H\textsubscript{2}O (0.1 mol/L) solution was quickly added into the mixture under vigorous stirring. The mixture was further stirred for 30 min to complete the reaction. Then, the precipitates were separated by centrifugation, washed with deionized water and absolute ethanol several times each, and dried in an oven at 60 °C for 4 h.
3.6 Typical procedures for the synthesis of 3H-1,2,4-triazine by polyhedron Cu$_2$O

A typical procedure for the synthesis of 3H-1,2,4-triazine (3) – *Synthesis of 3a*: a mixture of β-enaminone 1a (126 mg, 0.5 mmol), diazonium salt 2a (144 mg, 0.75 mmol), polyhedron Cu$_2$O (14 mg, 0.1 mmol), and K$_3$PO$_4$ (212 mg, 1.0 mmol) in 5 mL DMF was stirred at 80 °C for 1.0 h. The reaction mixture was cooled to ambient temperature, filtered through a short pad of celite, rinsed with 20 mL of ethyl acetate, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 15:1, v/v), affording 3a as a yellow liquid (115 mg, 65%).

3.7 X-Ray crystallographic studies

Single crystals for the X-ray diffraction studies for compounds 3k was carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1917695 for 3k. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).
Figure 1. Molecular structure of compound 3k.

Table S2. Crystal data and structure refinement for 3k.

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4. Analytical data for new compounds

(Z)-3-((4-methoxybenzyl)amino)-1-phenylbut-2-en-1-one (1d): 506 mg, yield 90%, yellow solid, m.p.: 104-106 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.69 (s, 1H), 7.87 (dd, $J = 7.7$, 1.8 Hz, 2H), 7.47-7.35 (m, 3H), 7.23 (dd, $J = 8.3$, 0.5 Hz, 2H), 6.98-6.81 (m, 2H), 5.74 (s, 1H), 4.47 (d, $J = 6.2$ Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 188.04, 164.91, 159.14, 140.41, 130.61, 129.78, 128.36, 128.26, 127.02, 114.37, 92.59, 55.41, 46.66, 19.64. HRMS (EI) calcd for C$_{18}$H$_{19}$NO$_2$ [M+H]$^+$: 282.1494; Found: 282.1484.

(Z)-3-((4-chlorobenzyl)amino)-1-phenylbut-2-en-1-one (1f): 456 mg, yield 80%, white solid, m.p.: 122-124 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.74 (s, 1H), 7.88 (dd, $J = 7.8$, 1.8 Hz, 2H), 7.46-7.37 (m, 3H), 7.35 -7.29 (m, 2H), 7.23 (d, $J = 8.5$, 2H), 5.77 (s, 1H), 4.49 (d, $J = 6.3$ Hz, 2H), 2.04 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 188.34, 164.78, 140.19, 136.40, 133.41, 130.75, 129.09, 128.28, 127.02, 92.89, 46.41, 19.53. HRMS (EI) calcd for C$_{17}$H$_{16}$ClNO [M+H]$^+$: 286.0999; Found: 286.1002.

(Z)-3-((4-bromobenzyl)amino)-1-phenylbut-2-en-1-one (1g): 579 mg, yield 88%, yellow solid, m.p.: 118-120 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 11.74 (s, 1H), 7.87 (dd, $J = 7.9$, 1.7 Hz, 2H), 7.48 (dd, $J = 8.4$, 0.2 Hz, 2H), 7.44-7.37 (m, 3H), 7.18 (d, $J = 8.4$ Hz, 2H), 5.77 (s, 1H), 4.49 (d, $J = 6.3$ Hz, 2H), 2.05 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 188.45, 164.81, 140.22, 136.98, 132.10, 130.80, 128.65, 128.33, 127.07, 121.53, 92.98, 46.51, 19.59. HRMS (EI) calcd for C$_{17}$H$_{16}$BrNO [M+H]$^+$: 330.0494; Found: 330.0499.
(Z)-3-((4-iodobenzyl)amino)-1-phenylbut-2-en-1-one (1h): 543 mg, yield 72%, white solid, m.p.: 101-103 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 11.73 (s, 1H), 7.87 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.47-7.34 (m, 3H), 7.06 (d, $J = 8.4$ Hz, 2H), 5.76 (s, 1H), 4.48 (d, $J = 6.3$ Hz, 2H), 2.04 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 188.44, 164.81, 140.22, 138.06, 137.69, 130.80, 128.89, 128.33, 127.08, 93.02, 92.98 46.60, 19.59. HRMS (EI) calcd for C$_{17}$H$_{16}$NO [M+H]$^+$: 378.0355; Found: 378.0355.

![Chemical structure](image)

(2)-3-((furan-2-ylmethyl)amino)-1-phenylbut-2-en-1-one (1i): 405 mg, yield 84%, yellow solid, m.p.: 50-52 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 11.59 (s, 1H), 7.86 (dd, $J = 7.9, 1.7$ Hz, 2H), 7.46-7.35 (m, 4H), 6.33 (t, $J = 3.2$ Hz, 1H), 6.26 (d, $J = 3.2$ Hz, 1H), 5.74 (s, 1H), 4.49 (d, $J = 6.2$ Hz, 2H), 2.16 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 188.31, 164.53, 150.97, 142.57, 140.28, 130.69, 128.26, 127.04, 110.53, 107.53, 92.94, 40.36, 19.47. HRMS (EI) calcd for C$_{15}$H$_{15}$NO$_2$ [M+H]$^+$: 242.1181; Found: 242.1183.

![Chemical structure](image)

(2)-1-phenyl-3-((thiophen-2-ylmethyl)amino)but-2-en-1-one (1j): 460 mg, yield 89%, yellow solid, m.p.: 61-63 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 11.69 (s, 1H), 7.88 (dd, $J = 7.9, 1.7$ Hz, 2H), 7.44-7.36 (m, 3H), 7.23-7.20 (m, 1H), 7.06-6.92 (m, 2H), 5.75 (s, 1H), 4.68 (d, $J = 6.2$ Hz, 2H), 2.12 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 188.35, 164.23, 140.82, 140.26, 130.71, 128.26, 127.17, 127.06, 125.45, 125.16, 92.95, 42.25, 19.49. HRMS (EI) calcd for C$_{15}$H$_{15}$NOS [M+H]$^+$: 258.0953; Found: 258.0953.

![Chemical structure](image)

(2)-3-((naphthalen-2-ylmethyl)amino)-1-phenylbut-2-en-1-one (1l): 542 mg, yield 90%, white solid, m.p.: 109-111 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 11.88 (s, 1H), 7.96-7.89 (m, 2H), 7.88-7.80 (m, 3H), 7.75 (s, 1H), 7.51-7.47 (m, 2H), 7.46-7.36 (m,
4H), 5.80 (s, 1H), 4.70 (d, J = 6.4 Hz, 2H), 2.09 (s, 3H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) δ 188.28, 165.09, 140.39, 135.38, 133.54, 132.89, 130.69, 128.87, 128.30, 127.93, 127.81, 127.08, 126.47, 126.10, 125.53, 125.03, 92.85, 47.27, 19.62. HRMS (EI) calcd for C$_{21}$H$_{19}$NO [M+H]+: 302.1545; Found: 302.1546.

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) δ 188.28, 165.09, 140.39, 135.38, 133.54, 132.89, 130.69, 128.87, 128.30, 127.93, 127.81, 127.08, 126.47, 126.10, 125.53, 125.03, 92.85, 47.27, 19.62. HRMS (EI) calcd for C$_{21}$H$_{19}$NO [M+H]+: 302.1545; Found: 302.1546.

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) δ 187.77, 165.18, 147.08, 145.78, 140.67, 134.58, 130.42, 128.21, 127.03, 126.95, 124.43, 124.09, 92.57, 55.40, 46.71, 38.36, 37.92, 37.16, 36.49, 33.58, 30.35, 25.54, 24.11, 19.78, 19.49, 18.73, 18.27. HRMS (EI) calcd for C$_{30}$H$_{39}$NO [M+H]+: 430.3110; Found: 430.3120.

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) δ 187.77, 165.18, 147.08, 145.78, 140.67, 134.58, 130.42, 128.21, 127.03, 126.95, 124.43, 124.09, 92.57, 55.40, 46.71, 38.36, 37.92, 37.16, 36.49, 33.58, 30.35, 25.54, 24.11, 19.78, 19.49, 18.73, 18.27. HRMS (EI) calcd for C$_{30}$H$_{39}$NO [M+H]+: 430.3110; Found: 430.3120.

$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) δ 187.77, 165.18, 147.08, 145.78, 140.67, 134.58, 130.42, 128.21, 127.03, 126.95, 124.43, 124.09, 92.57, 55.40, 46.71, 38.36, 37.92, 37.16, 36.49, 33.58, 30.35, 25.54, 24.11, 19.78, 19.49, 18.73, 18.27. HRMS (EI) calcd for C$_{30}$H$_{39}$NO [M+H]+: 430.3110; Found: 430.3120.
(5-methyl-3-phenyl-2-(p-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3b): 130 mg, yield 71%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97-7.87 (m, 2H), 7.60-7.52 (m, 1H), 7.48 (t, $J$ = 7.4 Hz, 2H), 7.39-7.29 (m, 5H), 7.21 (dd, $J$ = 8.5, 0.3 Hz, 2 H), 7.13 (dd, $J$ = 8.9, 0.4 Hz, 2H), 6.97 (s, 1H), 2.44 (s, 3H), 2.32 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.58, 156.77, 141.24, 138.13, 137.78, 137.23, 135.24, 132.05, 130.34, 130.02, 129.04, 128.75, 127.98, 126.11, 117.57, 73.06, 23.36, 20.88. HRMS (EI) calcld for C$_{24}$H$_{21}$N$_3$O [M+H]+: 368.1763; Found: 368.1767.

(5-methyl-3-phenyl-2-(m-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3c): 162 mg, yield 88%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96-7.87 (m, 2H), 7.61-7.53 (m, 1H), 7.52-7.45 (m, 2H), 7.37-7.31 (m, 5H), 7.23-7.14 (m, 2H), 7.09-7.06 (m, 1H), 6.99 (s, 1H), 6.98 (s, 1H), 2.42 (s, 3H), 2.32 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.65, 156.80, 143.53, 139.53, 138.05, 137.80, 137.23, 135.24, 132.05, 130.34, 129.04, 128.75, 127.98, 126.11, 117.57, 73.06, 23.33, 21.80. HRMS (EI) calcld for C$_{24}$H$_{21}$N$_3$O [M+H]+: 368.1763; Found: 368.1768.

(5-methyl-3-phenyl-2-(o-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3d): 117 mg, yield 64%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21-8.13 (m, 2H), 8.11 (s, 1H), 7.66 (dd, $J$ = 8.3, 1.2 Hz, 2H), 7.54 (t, $J$ = 7.4 Hz, 1H), 7.48-7.37 (m, 5H), 7.05 (d, $J$ = 7.4 Hz, 1H), 6.98 (t, $J$ = 7.7 Hz, 1H), 6.79 (t, $J$ = 7.3 Hz, 1H), 6.10 (d, $J$ = 8.0 Hz, 1H), 2.38 (s, 3H), 2.10 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)
\[ \delta \ 187.38, 149.94, 146.32, 145.09, 138.52, 132.94, 130.79, 130.11, 129.23, 128.74, 128.70, 128.60, 128.33, 127.19, 127.18, 123.93, 122.14, 111.75, 17.07, 16.59. \]

HRMS (EI) calcd for \( C_{24}H_{21}N_3O \) \([M+H]^+\): 368.1763; Found: 368.1768.

\((2-(4\text{-methoxyphenyl})-5\text{-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl})(\text{phenyl})\text{methanone (3e)}\): 135 mg, yield 70%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \ 8.02\text{-}7.75 \text{ (m, 2H)}, 7.59\text{-}7.51 \text{ (m, 1H)}, 7.50\text{-}7.43 \text{ (m, 2H)}, 7.40\text{-}7.29 \text{ (m, 5H)}, 7.23 \text{ (dd, } J = 7.1, 2.2 \text{ Hz, 2H)}, 6.92 \text{ (s, 1H)}, 6.85 \text{ (dd, } J = 7.0, 2.2 \text{ Hz, 2H)}, 3.76 \text{ (s, 3H)}, 2.43 \text{ (s, 3H)}; \ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (100 MHz, CDCl}_3\) \(\delta \ 189.56, 157.56, 156.71, 138.25, 137.80, 137.16, 136.98, 131.95, 130.27, 129.06, 128.78, 127.96, 126.08, 119.22, 114.64, 73.53, 55.60, 23.35. \) HRMS (EI) calcd for \( C_{24}H_{21}N_3O_2 \) \([M+H]^+\): 384.1712; Found: 384.1720.

\((2-(4\text{-fluorophenyl})-5\text{-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl})(\text{phenyl})\text{methanone (3f)}\): 136 mg, yield 73%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \ 7.94\text{-}7.82 \text{ (m, 2H)}, 7.60\text{-}7.54 \text{ (m, 1H)}, 7.52\text{-}7.45 \text{ (m, 2H)}, 7.39\text{-}7.30 \text{ (m, 5H)}, 7.25\text{-}7.21 \text{ (m, 2H)}, 7.06\text{-}6.98 \text{ (m, 2H)}, 6.91 \text{ (s, 1H)}, 2.40 \text{ (s, 3H)}; \ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (100 MHz, CDCl}_3\) \(\delta \ 189.62, 160.33 \text{ (d, } J = 247 \text{ Hz)}, 156.56, 139.84 \text{ (d, } J = 2.5 \text{ Hz)}, 137.96, 137.56, 137.49, 132.32, 130.33, 129.23, 129.01, 128.13, 126.10, 119.18 \text{ (d, } J = 8.2 \text{ Hz)}, 116.32 \text{ (d, } J = 22.9 \text{ Hz)}, 73.36, 23.34. \) HRMS (EI) calcd for \( C_{23}H_{18}FN_3O \) \([M+H]^+\): 372.1512; Found: 372.1521.

\((2-(4\text{-chlorophenyl})-5\text{-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl})(\text{phenyl})\text{methanone (3g)}\): 135 mg, yield 70%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \ 7.67\text{-}7.55 \text{ (m, 2H)}, 7.52\text{-}7.45 \text{ (m, 2H)}, 7.39\text{-}7.30 \text{ (m, 5H)}, 7.25\text{-}7.21 \text{ (m, 2H)}, 7.06\text{-}6.98 \text{ (m, 2H)}, 6.91 \text{ (s, 1H)}, 2.40 \text{ (s, 3H)}; \ ^{13}\text{C}\{^{1}\text{H}\} \text{NMR (100 MHz, CDCl}_3\) \(\delta \ 189.62, 160.33 \text{ (d, } J = 247 \text{ Hz)}, 156.56, 139.84 \text{ (d, } J = 2.5 \text{ Hz)}, 137.96, 137.56, 137.49, 132.32, 130.33, 129.23, 129.01, 128.13, 126.10, 119.18 \text{ (d, } J = 8.2 \text{ Hz)}, 116.32 \text{ (d, } J = 22.9 \text{ Hz)}, 73.36, 23.34. \) HRMS (EI) calcd for \( C_{23}H_{18}FN_3O \) \([M+H]^+\): 372.1512; Found: 372.1521.
(2-(3-chlorophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3g): 130 mg, yield 67%, yellow liquid. $^1$H NMR (400 MHz,CDCl$_3$) $\delta$ 7.86 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.59-7.51 (m, 1H), 7.48-7.43 (m, 2H), 7.35-7.27 (m, 5H), 7.25-7.23 (m, 2 H), 7.17 (dd, $J = 7.0, 2.0$ Hz, 2H), 6.90 (s, 1H), 2.37 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.59, 156.53, 142.06, 137.80, 137.55, 137.44, 132.45, 130.62, 130.35, 129.57, 129.25, 129.05, 128.16, 126.09, 118.54, 72.92, 23.35. HRMS (EI) calcd for C$_{23}$H$_{18}$ClN$_3$O [M+H]$^+$: 388.1217; Found: 388.1227.

(2-(4-bromophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3j): 125 mg, yield 58%, yellow liquid. $^1$H NMR (400 MHz,CDCl$_3$) $\delta$ 7.89 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.63-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.36-7.32 (m, 6H), 7.23 (t, $J = 8.1$ Hz, 1H), 7.12-7.09 (m, 2H), 6.93 (s, 1H), 2.40 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.59, 156.52, 142.54, 137.77, 137.56, 137.41, 132.50, 132.47, 130.36, 129.26, 129.06, 128.17, 126.08, 118.84, 118.29, 72.83, 23.37. HRMS (EI) calcd for C$_{23}$H$_{18}$BrN$_3$O [M+H]$^+$: 432.0711; Found: 432.0706.
(3-(4-bromophenyl)-3,5-diphenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3k): 128 mg, yield 52%, yellow solid, m.p.: 193-195 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (dd, $J = 8.1$, 0.9 Hz, 2H), 7.51-7.39 (m, 6H), 7.38-7.27 (m, 8H), 7.26-7.22 (m, 2H), 7.20 (s, 1H); $^{13}$C{^1}H NMR (100 MHz, CDCl$_3$) δ 188.09, 157.87, 142.63, 139.72, 136.62, 136.30, 136.26 133.03, 132.57, 130.44, 130.21, 129.18, 129.05, 128.43, 128.35, 128.10, 126.33, 119.09, 118.33, 73.02. HRMS (EI) calcd for C$_{28}$H$_{20}$BrN$_3$O [M+H]$^+$: 494.0868; Found: 494.0869.

(5-methyl-2-phenyl-3-(p-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3l): 142 mg, yield 77%, yellow liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (dd, $J = 8.3$, 1.3 Hz, 2H), 7.62-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.38-7.31 (m, 4H), 7.28 (d, $J = 2.5$ Hz, 2H), 7.18-7.14 (m, 3H), 6.98 (s, 1H), 2.44 (s, 3H), 2.35 (s, 3H); $^{13}$C{^1}H NMR (100 MHz, CDCl$_3$) δ 189.62, 156.43, 143.47, 138.70, 138.01, 137.38, 134.83, 132.16, 130.36, 129.76, 129.43, 128.03, 126.03, 125.15, 117.50, 72.85, 23.36, 21.24. HRMS (EI) calcd for C$_{24}$H$_{21}$N$_3$O [M+H]$^+$: 368.1763; Found: 368.1770.

(3-(4-methoxyphenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3m): 135 mg, yield 70%, yellow liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (dd, $J = 8.3$, 1.3 Hz, 2H), 7.63-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.35-7.28 (m, 5H), 7.27-7.26 (m, 1H), 7.18-7.12 (m, 1H), 6.93 (s, 1H), 6.86 (dd, $J = 7.5$, 2.0 Hz, 2H), 3.77 (s, 3H), 2.42 (s, 3H); $^{13}$C{^1}H NMR (100 MHz, CDCl$_3$) δ 189.64, 159.98, 156.38, 143.47, 137.99, 137.33, 132.19, 130.38, 129.95, 129.46,
HRMS (EI) calcd for C_{24}H_{21}N_{3}O_{2} [M+H]^+: 384.1712; Found: 384.1720.

(3-(4-fluorophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3n): 117 mg, yield 63%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.92\) (dd, \(J = 8.4, 1.3\) Hz, 2H), 7.63-7.54 (m, 1H), 7.51-7.46 (m, 2H), 7.36-7.27 (m, 6H), 7.19-7.15 (m, 1H), 7.05-6.99 (m, 2H), 6.96 (s, 1H), 2.41 (s, 3H); \(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 189.55, 162.94\) (d, \(J = 248\) Hz), 156.92, 143.36, 137.79, 133.77, 133.51 (d, \(J = 3.4\) Hz), 132.36, 130.39, 129.58, 128.13, 128.05 (d, \(J = 8.5\) Hz), 125.36, 117.48, 116.11 (d, \(J = 21.7\) Hz), 72.22, 23.26. HRMS (EI) calcd for C\(_{23}\)H\(_{18}\)F\(_3\)N\(_3\)O \([M+H]^+\): 372.1512; Found: 372.1520.

(3-(4-chlorophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3o): 95 mg, yield 49%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.92\) (dd, \(J = 8.4, 1.3\) Hz, 2H), 7.63-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.37-7.26 (m, 8H), 7.20-7.15 (m, 1H), 6.96 (s, 1H), 2.41 (s, 3H); \(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 189.47, 157.09, 143.30, 137.85, 137.74, 136.11, 134.80, 132.37, 130.37, 129.58, 129.31, 128.12, 127.62, 125.39, 117.45, 72.20, 23.24. HRMS (EI) calcd for C\(_{23}\)H\(_{18}\)Cl\(_3\)N\(_3\)O \([M+H]^+\): 388.1217; Found: 388.1227.

(3-(4-bromophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3p): 128 mg, yield 59%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.91\) (dd, \(J = 8.3, 1.3\) Hz, 2H), 7.62-7.54 (m, 1H), 7.53-7.44 (m, 4H), 7.45-7.36 (m, 2H), 7.19-7.15 (m, 1H), 6.95 (s, 1H), 2.41 (s, 3H); \(^{13}\)C\(\{^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta 189.39, 157.09, 143.30, 137.85, 137.74, 136.11, 134.80, 132.37, 130.37, 129.58, 129.31, 128.12, 127.62, 125.39, 117.45, 72.20, 23.24. HRMS (EI) calcd for C\(_{23}\)H\(_{18}\)Br\(_3\)N\(_3\)O \([M+H]^+\): 394.1117; Found: 394.1127.
7.37-7.32 (m, 2H), 7.30-7.26 (m, 2H), 7.23-7.19 (m, 2H), 7.18-7.15 (m, 1H), 6.93 (s, 1H), 2.40 (s, 3H); $^{13}$C {$^{1}$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.50, 157.16, 143.31, 137.89, 137.74, 136.62, 132.41, 132.29, 130.39, 129.61, 128.15, 127.93, 125.43, 123.00, 117.47, 72.28, 23.26. HRMS (EI) calcd for C$_{23}$H$_{18}$BrN$_3$O [M+H]$^+$: 432.0711; Found: 432.0706.

(3-(4-iodophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3q): 126 mg, yield 53%, red liquid. $^1$H NMR (400 MHz,CDCl$_3$) $\delta$ 7.91 (dd, $J$ = 8.3, 1.2 Hz, 2H), 7.69-7.65 (m, 2H), 7.60-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.35-7.30 (m, 2H), 7.28 (d, $J$ = 1.2 Hz, 2H), 7.19-7.15 (m, 1H), 7.08 (dd, $J$ = 8.7, 0.5 Hz, 2H), 6.92 (s, 1H), 2.40 (s, 3H); $^{13}$C {$^{1}$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.47, 157.14, 143.29, 138.22, 137.86, 137.73, 137.28, 132.38, 130.38, 129.59, 128.14, 128.07, 125.41, 117.45, 94.74, 72.35, 23.25. HRMS (EI) calcd for C$_{23}$H$_{18}$IN$_3$O [M+H]$^+$: 480.0573; Found: 480.0583.

(3-(furan-2-yl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3r): 104 mg, yield 61%, yellow solid, m.p.: 144-146 °C. $^1$H NMR (400 MHz,CDCl$_3$) $\delta$ 7.91 (dd, $J$ = 8.4, 1.3 Hz, 2H), 7.58-7.52 (m, 1H), 7.51-7.43 (m, 4H), 7.42-7.33 (m, 3H), 7.20 (t, $J$ = 7.3 Hz, 1H), 7.04 (s, 1H), 6.31 (d, $J$ = 1.2 Hz, 2H), 2.52 (s, 3H); $^{13}$C {$^{1}$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.69, 159.07, 149.13, 143.79, 143.21, 138.81, 137.76, 132.32, 130.41, 129.48, 128.08, 125.43, 118.15, 110.96, 110.61, 66.68, 23.13. HRMS (EI) calcd for C$_{21}$H$_{17}$N$_3$O$_2$ [M+H]$^+$: 344.1399; Found: 344.1408.
(5-methyl-2-phenyl-3-(thiophen-2-yl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3s): 105 mg, yield 58%, red solid, m.p.: 157-159 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (dd, \(J = 8.4, 1.3\) Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 4H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), 7.21-7.16 (m, 1H), 6.99 (d, \(J = 3.5\) Hz, 1H), 6.93 (t, \(J = 4.4\) Hz, 1H), 2.49 (s, 3H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 189.67, 158.26, 143.03, 139.76, 138.42, 137.82, 132.34, 130.41, 129.62, 128.08, 126.82, 126.65, 126.52, 125.43, 117.76, 68.73, 23.20. HRMS (EI) calcd for C\(_{21}\)H\(_{17}\)N\(_3\)OS [M+H]\(^+\): 360.1171; Found: 360.1180.

(5-methyl-2-phenyl-3-(pyridin-2-yl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3t): 99 mg, yield 56%, yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.63-8.54 (m, 1H), 7.94 (dd, \(J = 8.3, 1.3\) Hz, 2H), 7.70-7.64 (m, 1H), 7.58-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.17-7.10 (m, 1H), 7.05 (s, 1H), 2.47 (s, 3H). \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 189.75, 157.47, 156.74, 150.02, 143.49, 137.99, 137.26, 136.97, 132.21, 130.47, 129.32, 128.02, 125.20, 123.76, 121.51, 117.84, 74.12, 23.42. HRMS (EI) calcd for C\(_{22}\)H\(_{18}\)N\(_4\)O [M+H]\(^+\): 355.1559; Found: 355.1569.

(5-methyl-3-(naphthalen-2-yl)-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3u): 134 mg, yield 66%, orange liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (dd, \(J = 8.4, 1.3\) Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 4H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), 7.21-7.16 (m, 1H), 6.99 (d, \(J = 3.5\) Hz, 1H), 6.93 (t, \(J = 4.4\) Hz, 1H), 2.49 (s, 3H); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\)) \(\delta\) 189.67, 158.26, 143.03, 139.76, 138.42, 137.82, 132.34, 130.41, 129.62, 128.08, 126.82, 126.65, 126.52, 125.43, 117.76, 68.73, 23.20. HRMS (EI) calcd for C\(_{27}\)H\(_{21}\)N\(_3\)O [M+H]\(^+\): 404.1763; Found: 404.1773.
1-(5-methyl-2,3-diphenyl-2,3-dihydro-1,2,4-triazin-6-yl)ethan-1-one (3v): 111 mg, yield 76%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.37 (m, 4H), 7.36-7.27 (m, 5H), 7.24-7.21 (m, 1H), 6.91 (s, 1H), 2.49 (s, 3H), 2.38 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 194.99, 156.27, 143.51, 138.23, 137.51, 129.53, 129.07, 128.81, 126.08, 125.62, 117.84, 73.22, 25.71, 23.96. HRMS (EI) calcd for C$_{18}$H$_{17}$N$_3$O [M+H]$^+$: 292.1450; Found: 292.1455.

(3-(ethylamino)-1-phenyl-1H-pyrazol-3-yl)(phenyl)methanone (4a): 53 mg, yield 36%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (dd, $J$ = 8.4, 1.3 Hz, 2H), 7.75 (dd, $J$ = 8.6, 1.1 Hz, 2H), 7.60-7.54 (m, 1H), 7.52-7.44 (m, 4H), 7.40 (s, 1H), 7.35-7.30 (m, 1H), 5.81 (t, $J$= 4.88 Hz, 1H), 3.19 (q, $J$ = 5.52 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 189.36, 141.50, 140.21, 138.24, 138.04, 132.26, 130.54, 129.56, 128.17, 127.14, 119.29, 108.98, 40.99, 14.90. HRMS (EI) calcd for C$_{18}$H$_{17}$N$_3$O [M+H]$^+$: 292.1450; Found: 292.1454.

(3-(((1S,4aR,10aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-1-phenyl-1H-pyrazol-3-yl)(phenyl)methanone (4b): 101 mg, yield 38%, yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (dd, $J$ = 8.4, 1.3 Hz, 2H), 7.75 (dd, $J$ = 8.5, 1.0 Hz, 2H), 7.58-
7.53 (m, 1H), 7.52-7.45 (m, 4H), 7.39 (s, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 8.2 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.89 (s, 1H), 6.14 (t, J = 6.4 Hz, 1H), 3.10-3.05 (m, 1H), 2.97-2.88 (m, 3H), 2.86-2.78 (m, 1H), 2.35-2.27 (m, 1H), 2.01-1.75 (m, 3H), 1.74-1.65 (m, 2H), 1.64-1.61 (m, 1H), 1.58 (s, 2H), 1.26 (s, 3H), 1.24-1.20 (m, 6H), 1.06 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 189.47, 147.33, 145.66, 142.79, 140.22, 138.26, 137.89, 134.82, 132.21, 130.51, 129.55, 128.14, 127.13, 126.98, 124.50, 124.02, 119.30, 108.57, 58.71, 46.06, 38.51, 37.96, 37.73, 36.59, 33.59, 30.55, 25.60, 24.13, 19.36, 18.97, 18.93. HRMS (EI) calcd for C$_{36}$H$_{41}$N$_3$O [M+H]$^+$: 532.3328; Found: 532.3338.

3-(benzylimino)-1-phenyl-2-(2-phenylhydrazono)butan-1-one (5): 169 mg, yield 95%, yellow liquid. $^1$H NMR (400 MHz,CDCl$_3$) δ 15.81 (s, 1H), 7.89 (d, J = 7.6, 1.0 Hz, 2H), 7.56-7.38 (m, 8H), 7.23 (dd, J = 8.1, 0.7 Hz, 2H), 7.10-7.04 (m, 3H), 4.75 (s, 2H), 2.53 (s, 3H); $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$) δ 193.53, 164.83, 146.93, 140.16, 138.16, 131.57, 131.24, 130.56, 129.26, 129.07, 127.83, 127.78, 127.60, 125.17, 117.64, 51.87, 17.72. HRMS (EI) calcd for C$_{23}$H$_{21}$N$_3$O [M+H]$^+$: 356.1763; Found: 356.1769.
5. Copies of NMR spectra for compounds