Selective N-N or N-S bond cleavage of 1-trifluoromethyl benzotriazoles enables divergent synthesis of 1,2,4-benzotriazines and benzotriazoles

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1. General Information

$^1$H and $^{13}$C spectra were measured on a 600 MHz or 400 MHz NMR spectrometer using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million relatives to TMS, and the coupling constants are given in hertz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with an APCI or ESI, EI source. Single-crystal X-ray diffraction studies were conducted at 293 K on the Bruker D8 VENTURE diffractometer equipped with a PHOTON-II detector (MoKα, $\lambda = 0.71073$ Å). An oil bath was used for heating when was needed. Column chromatography was performed using silica gel (200-300 mesh).

Commercially available materials purchased from Bidepharm and Energy Chemical were used as received. Unless otherwise specified, all reactions were carried out under nitrogen atmosphere in 10 mL Schlenk tubes. Benzotriazole were prepared according to previous literature procedures.
2. Optimization of reaction conditions for the synthesis of 5a

The results of the optimization of reaction conditions for the synthesis of 5a are shown in Table S1. Different solvents were studied for the transformation mediated by LiOH (entries 1-5), and the reaction in DMF was found to be more effective than others (entry 3). Then different bases were also screened. The yield of 5a was decreased when KOH, DBU or t-BuOK was utilized (entries 6-8). However, the use of Cs₂CO₃ afforded a better result (entry 9). Further investigation indicated that 1,4-dioxane was the most suitable solvent for the reaction mediated by Cs₂CO₃ (entry 14 vs entries 9-13). Therefore, the optimal reaction conditions for the synthesis of 5a was established as following: using Cs₂CO₃ (2.0 eq) as the base and 1,4-dioxane as the solvent, and being stirred at room temperature.

Table S1  Optimization of reaction conditions for the synthesis of 5a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield of 5a (%)</th>
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<td>1</td>
<td>LiOH</td>
<td>THF</td>
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<tr>
<td>2</td>
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<td>4</td>
<td>LiOH</td>
<td>MeCN</td>
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</tr>
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<td>LiOH</td>
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<td>6</td>
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<td>7</td>
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<td>8</td>
<td>t-BuOK</td>
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<tr>
<td>9</td>
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<td>14</td>
<td>Cs₂CO₃</td>
<td>1,4-dioxane</td>
<td>80</td>
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</table>

*Reaction conditions: a mixture of 1-Tf-substituted benzotriazole 1a (0.20 mmol), α-bromoacetophenone 4a (0.40 mmol, 2 equiv), and base (0.40 mmol, 2 equiv) was stirred at rt under air atmosphere for about 6 h (monitored by TLC). *Yields of the products approximately determined by the crude ¹H NMR spectra. *nd = no desired product was detected. Yields of isolated products.*
3. General procedure for the synthesis of products 3 and 5

3.1 General procedure for the synthesis of products 3

Under nitrogen atmosphere, in a dry Schlenk tube, benzotriazole 1 (0.20 mmol) was added to tetrahydrofuran (2.0 mL) and stirred at room temperature. Then, bromide 2 (0.4 mmol) and LiOH (9.6 mg, 0.4 mmol) were added in sequence. The mixture was stirred for 6 h at room temperature. When the reaction was completed (monitored by TLC). The mixture was directly concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 20:1) to afford the desired product 3 in good yields.

3.2 General procedure for the synthesis of products 5

In a dry Schlenk tube, benzotriazole 1 (0.20 mmol) was added to 1,4-dioxane (2.0 mL) and stirred at room temperature. Then, bromide 4 (0.4 mmol) and Cs₂CO₃ (130.33mg, 0.4 mmol) were added in sequence. The mixture was stirred 6 h at room temperature. When the reaction was completed (monitored by TLC). The mixture was directly concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 20:1) to afford the desired product 5 in good yields.
4. General procedure for the transformations of 3p

\[
\begin{align*}
\text{Under nitrogen atmosphere, in a dry Schlenk tube with a magnetic stir bar, was added 3p (72.2 mg, 0.20 mmol) and the reaction solvent Et}_3\text{N (2.0 mL) were added, followed by Pd(PPh}_3\text{)}_2\text{Cl}_2 (7.0 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol), 10 min later by p-methoxyphenylacetylene (29.07 mg, 0.22 mmol) and the reaction mixture was stirred at 60°C for 12 h until the 3p was complete consumed (monitored by TLC). The reaction was quenched with HCl (1.0 M, pH = 6-7), and extracted with EA (10 mL×3). The organic extracts were combined and dried over Na}_2\text{SO}_4 \text{ and concentrated under reduced pressure. The resulting crude residue was purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford the desired product 6 with 90% (65.7 mg) yield.}
\end{align*}
\]

\[
\begin{align*}
\text{Under nitrogen atmosphere, in a dry Schlenk tube with a magnetic stir bar, was added 6 (73.0 mg, 0.20 mmol) and the reaction solvent PhCl (2.0 mL) were added, the reaction mixture was stirred at 160°C for 24 h until the 6 was complete consumed (monitored by TLC). The system was cooled to room temperature and the solvent was spin-dried over the column (petroleum ether/ethyl acetate = 8:1) to afford the desired product 7 with 75% (50.6 mg) yield.}
\end{align*}
\]
5. Crystal structures of 5e

Product 5e was crystallized as a yellow crystal via vaporization of a petroleum ether/ethyl acetate solution, and its absolute configuration was determined by x-ray structure analysis. The CCDC number was 2241694. The supplementary crystallographic data that could be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

![Crystal structure of 5e](image)
Crystal data and structure refinement for 5e.

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<td>Independent reflections</td>
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<td>Final R indexes [all data]</td>
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<td>Largest diff. peak/hole / e Å-3</td>
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</table>
6. Characterization of Products

Benzo[e][1,2,4]triazin-3-yl(phenyl)methanone (3a)

Isolated in 78% yield (36.7 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (dd, J = 8.4, 0.8 Hz, 1H), 8.26 – 8.19 (m, 1H), 8.14 – 8.08 (m, 3H), 8.06 – 8.01 (m, 1H), 7.69 – 7.63 (m, 1H), 7.55 – 7.48 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.55, 158.10, 147.60, 140.33, 136.65, 135.16, 134.24, 132.73, 131.23, 129.80, 129.68, 128.69. HRMS (ESI) calcd. for C$_{14}$H$_{10}$N$_3$O [M+H$^+$]: 236.0810, found: 236.0819.

(8-Methylbenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3b)

Isolated in 67% yield (33.4 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 – 8.13 (m, 2H), 8.08 (d, J = 8.5 Hz, 1H), 8.03 – 7.97 (m, 1H), 7.85 – 7.81 (m, 1H), 7.71 – 7.64 (m, 1H), 7.57 – 7.51 (m, 2H), 3.11 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.80, 158.00, 146.89, 140.97, 139.40, 136.79, 135.39, 134.13, 132.45, 131.32, 128.60, 127.40, 17.02. HRMS (ESI) calcd. for C$_{15}$H$_{12}$N$_3$O [M+H$^+$]: 250.0975, found: 250.0976.

(8-Fluorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3c)

Isolated in 65% yield (32.9 mg) as yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.15 – 8.05 (m, 4H), 7.74 – 7.66 (m, 2H), 7.60 – 7.50 (m, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 190.08 (s), 158.56 (s), 157.74 (d, J = 270.2 Hz), 141.04 (s), 139.23 (d, J = 12.5 Hz), 136.68 (d, J = 8.4 Hz), 134.95 (s), 134.47 (s), 131.25 (s), 128.79 (s), 125.66 (d, J = 5.2 Hz), 116.45 (d, J = 17.7 Hz). HRMS (ESI) calcd. for C$_{14}$H$_9$FN$_3$O [M+H$^+$]: 254.0724, found: 254.0724.

(7-Chlorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3d)
Isolated in 67% yield (36.1 mg) as yellow solid.

\[ \text{^1H NMR (400 MHz, CDCl}_3 \text{)} \delta 8.68 (d, J = 1.9 \text{ Hz}, 1H), 8.22 (d, J = 9.0 \text{ Hz}, 1H), 8.12 (d, J = 7.5 \text{ Hz}, 2H), 8.05 (dd, J = 9.0, 2.1 \text{ Hz}, 1H), 7.72 – 7.65 (m, 1H), 7.58 – 7.52 (m, 2H). \text{^13C NMR (101 MHz, CDCl}_3 \text{)} \delta 190.17, 158.19, 147.52, 139.12, 138.98, 137.97, 135.08, 134.41, 131.27, 128.79, 128.41 (1 peak is missing). HRMS (ESI) calcd. for C\textsubscript{14}H\textsubscript{9}ClN\textsubscript{3}O [M+H\textsuperscript+]: 270.0429, found: 270.0431.\]

(6-Methylbenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3e)

Isolated in 69% yield (34.4 mg) as yellow solid.

\[ \text{^1H NMR (600 MHz, CDCl}_3 \text{)} \delta 8.53 (d, J = 8.6 \text{ Hz}, 1H), 8.12 (d, J = 7.6 \text{ Hz}, 2H), 7.98 (s, 1H), 7.86 (d, J = 8.5 \text{ Hz}, 1H), 7.71 – 7.63 (m, 1H), 7.58 – 7.49 (m, 2H), 2.70 (s, 3H). \text{^13C NMR (151 MHz, CDCl}_3 \text{)} \delta 190.71, 158.29, 148.63, 146.62, 140.69, 135.31, 135.29, 134.13, 131.22, 129.26, 128.63, 127.86, 22.79. HRMS (ESI) calcd. for C\textsubscript{15}H\textsubscript{12}N\textsubscript{3}O [M+H\textsuperscript+]: 250.0975, found: 250.0976. \]

(6-Fluorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3f)

Isolated in 78% yield (39.5 mg) as yellow solid.

\[ \text{^1H NMR (600 MHz, CDCl}_3 \text{)} \delta 8.74 – 8.68 (m, 1H), 8.12 – 8.07 (m, 2H), 7.84 – 7.79 (m, 2H), 7.70 – 7.65 (m, 1H), 7.55 – 7.51 (m, 2H). \text{^13C NMR (151 MHz, CDCl}_3 \text{)} \delta 190.27, 166.64 (d, J = 264.1 \text{ Hz}), 158.39, 145.61, 142.28 (d, J = 14.8 \text{ Hz}), 135.01, 134.41, 132.96 (d, J = 10.9 \text{ Hz}), 131.22, 128.77, 124.19 (d, J = 27.3 \text{ Hz}), 112.82 (d, J = 21.9 \text{ Hz}). HRMS (ESI) calcd. for C\textsubscript{14}H\textsubscript{9}FN\textsubscript{3}O [M+H\textsuperscript+]: 254.0724, found: 254.0726. \]

(6-Chlorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3g)

Isolated in 58% yield (31.2 mg) as yellow solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.63 (d, \(J = 9.0\) Hz, 1H), 8.23 (d, \(J = 2.0\) Hz, 1H), 8.14 – 8.06 (m, 2H), 7.97 (dd, \(J = 9.0, 2.1\) Hz, 1H), 7.73 – 7.65 (m, 1H), 7.59 – 7.48 (m, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 190.20, 158.56, 146.26, 143.37, 140.86, 134.99, 134.45, 134.19, 131.24, 131.19, 128.80, 128.40. HRMS (ESI) calcd. for C\(_{14}\)H\(_9\)ClN\(_3\)O [M+H\(^+\)]: 270.0429, found: 270.0431.

(6,7-Dimethylbenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3h)

Isolated in 63% yield (33.2 mg) as yellow solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.36 (s, 1H), 8.12 (dd, \(J = 8.4, 1.2\) Hz, 2H), 7.95 (s, 1H), 7.69 – 7.62 (m, 1H), 7.53-7.50 (m, 2H), 2.61 (s, 3H), 2.59 (s, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 190.80, 157.80, 148.92, 146.91, 144.35, 139.63, 135.37, 133.94, 131.19, 128.51, 128.07, 128.01, 21.23, 20.80. HRMS (ESI) calcd. for C\(_{16}\)H\(_{14}\)N\(_3\)O [M+H\(^+\)]: 264.1131, found: 264.1131.

(6,7-Difluorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3i)

Isolated in 55% yield (29.8 mg) as yellow solid.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.42 (t, \(J = 8.4\) Hz, 1H), 8.09 (d, \(J = 7.5\) Hz, 2H), 8.02 – 7.93 (m, 1H), 7.69 (t, \(J = 7.7\) Hz, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 189.91, 158.33 (d, \(J = 2.4\) Hz), 157.12 (dd, \(J = 269.4, 16.9\) Hz), 153.99 (dd, \(J = 265.7, 17.0\) Hz), 145.54 (d, \(J = 10.4\) Hz), 139.15 (d, \(J = 12.6\) Hz), 134.91, 134.45, 131.19, 128.77, 115.47 (d, \(J = 2.3\) Hz), 115.34 (dd, \(J = 9.8, 7.8\) Hz). HRMS (ESI) calcd. for C\(_{16}\)H\(_8\)F\(_2\)N\(_3\)O [M+H\(^+\)]: 272.0630, found: 272.0639.

(6,7-Dichlorobenzo[e][1,2,4]triazin-3-yl)(phenyl)methanone (3j)

Isolated in 57% yield (34.5 mg) as yellow solid.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.81 (s, 1H), 8.37 (s, 1H), 8.09 (d, \(J = 7.7\) Hz, 2H), 7.71 – 7.67 (m, 1H), 7.54 (t, \(J = 7.7\) Hz, 2H). \(^1\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 189.86, 158.44, 146.09, 142.57, 139.10, 138.18, 134.90, 134.53, 131.22, 130.34, 130.19, 128.83. HRMS (ESI) calcd. for C\(_{14}\)H\(_8\)Cl\(_2\)N\(_3\)O [M+H\(^+\)]: 304.0039, found: 304.0042.
Benzo[e][1,2,4]triazin-3-yl(2-methoxyphenyl)methanone (3k)

Isolated in 60% yield (31.8 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.63 (dd, $J = 8.4$, 0.7 Hz, 1H), 8.23 (d, $J = 8.1$ Hz, 1H), 8.11 – 8.04 (m, 1H), 8.02 – 7.94 (m, 2H), 7.63 – 7.56 (m, 1H), 7.19 – 7.13 (m, 1H), 6.95 (d, $J = 8.4$ Hz, 1H), 3.41 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 192.09, 159.84, 159.46, 147.31, 140.74, 136.15, 135.29, 132.06, 131.53, 129.82, 129.76, 126.51, 121.37, 112.01, 55.81. HRMS (ESI) calcd. for C$_{15}$H$_{12}$N$_3$O$_2$ [M+H$^+$]: 266.0924, found: 266.0925.

Benzo[e][1,2,4]triazin-3-yl(4-methoxyphenyl)methanone (3l)

Isolated in 56% yield (29.7 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (d, $J = 8.3$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 8.18 – 8.08 (m, 3H), 8.07 – 7.99 (m, 1H), 7.01 (d, $J = 8.9$ Hz, 2H), 3.92 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.98, 164.64, 158.70, 147.62, 140.47, 136.54, 133.84, 132.51, 129.86, 129.72, 114.12, 55.76. HRMS (ESI) calcd. for C$_{15}$H$_{12}$N$_3$O$_2$ [M+H$^+$]: 266.0924, found: 266.0926.

Benzo[e][1,2,4]triazin-3-yl(4-fluorophenyl)methanone (3m)

Isolated in 64% yield (32.4 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.69 (dd, $J = 8.4$, 0.5 Hz, 1H), 8.29 – 8.19 (m, 3H), 8.17 – 8.12 (m, 1H), 8.10 – 8.04 (m, 1H), 7.26 – 7.19 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.86, 166.52 (d, $J = 257.3$ Hz), 157.87, 144.04 (d, $J = 731.1$ Hz), 136.78, 134.20, 133.50 (d, $J = 121.9$ Hz), 131.65 (d, $J = 3.0$ Hz), 129.87, 129.74, 116.14, 115.92. HRMS (ESI) calcd. for C$_{14}$H$_9$FN$_3$O [M+H$^+$]: 254.0724, found: 254.0726.

Benzo[e][1,2,4]triazin-3-yl(3-chlorophenyl)methanone (3n)

Isolated in 57% yield (30.7 mg) as yellow solid.
Benzo[e][1,2,4]triazin-3-yl(2-bromophenyl)methanone (3o)

Isolated in 59% yield (36.9 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J = 8.3$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 8.16 – 8.10 (m, 1H), 8.07 (t, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.86, 156.67, 147.25, 142.63, 140.74, 139.85, 136.65, 133.22, 132.75, 131.09, 130.02, 129.80, 128.29, 93.47. HRMS (ESI) calcd. for C$_{14}$H$_9$BrN$_3$O $[M+H^+]$: 313.9924, found: 313.9926.

Benzo[e][1,2,4]triazin-3-yl(2-iodophenyl)methanone (3p)

Isolated in 60% yield (43.3 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J = 8.3$ Hz, 1H), 8.26 (d, $J = 8.4$ Hz, 1H), 8.13 (t, $J = 7.5$ Hz, 1H) 8.07 (t, $J = 7.6$ Hz, 1H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.77, 155.94, 147.25, 142.63, 140.70, 139.85, 136.65, 133.22, 132.75, 131.09, 130.02, 129.80, 128.29, 93.47. HRMS (ESI) calcd. for C$_{14}$H$_9$I$_2$N$_3$O $[M+H^+]$: 361.9785, found: 361.9786.

Benzo[e][1,2,4]triazin-3-yl(3,4-dichlorophenyl)methanone (3q)

Isolated in 77% yield (46.7 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (dd, $J = 8.4$, 0.7 Hz, 1H), 8.30 (d, $J = 2.0$ Hz, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 8.18 – 8.13 (m, 1H), 8.11 – 8.02 (m, 2H), 7.63 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$)
δ 188.14, 157.10, 147.75, 140.41, 139.02, 136.97, 134.86, 133.45, 133.23, 133.08, 130.86, 130.33, 129.92, 129.83. HRMS (ESI) calcd. for C_{14}H_{8}Cl_{2}N_{3}O [M+H^+]: 304.0039, found: 304.0041.

(5-Bromo-2-chlorophenyl)(7-methylbenzo[e][1,2,4]triazin-3-yl)methanone (3r)

Isolated in 56% yield (40.4 mg) as yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.41 (s, 1H), 8.16 (d, $J$ = 8.7 Hz, 1H), 7.96 (dd, $J$ = 8.7, 1.4 Hz, 1H), 7.89 (d, $J$ = 2.3 Hz, 1H), 7.65 (dd, $J$ = 8.5, 2.3 Hz, 1H), 7.32 (d, $J$ = 8.5 Hz, 1H), 2.73 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.93, 156.16, 147.47, 145.00, 139.50, 139.45, 138.83, 135.70, 133.66, 131.89, 131.64, 129.48, 128.07, 120.98, 22.47. HRMS (ESI) calcd. for C$_{15}$H$_{10}$BrClN$_3$O [M+H$^+$]: 361.9690, found: 361.9695.

Ethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)acetate (5a)

Isolated in 80% yield (32.8 mg) as yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 – 8.04 (m, 1H), 7.52 – 7.43 (m, 2H), 7.40 – 7.34 (m, 1H), 5.40 (s, 2H), 4.22 (q, $J$ = 7.1 Hz, 2H), 1.24 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.45, 146.06, 133.45, 127.97, 124.18, 120.21, 109.33, 62.39, 49.14, 14.12. HRMS (ESI) calcd. for C$_{10}$H$_{12}$N$_3$O$_2$ [M+H$^+$]: 206.0924, found: 206.0921.

Ethyl 2-(5,6-dimethyl-1H-benzo[d][1,2,3]triazol-1-yl)acetate (5b)

Isolated in 66% yield (30.8 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.21 (s, 1H), 5.35 (s, 2H), 4.25 (q, $J$ = 7.1 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.26 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.68, 145.35, 138.49, 134.08, 132.56, 119.36, 108.76, 62.37, 49.16, 21.11, 20.53, 14.21. HRMS (ESI) calcd. for C$_{12}$H$_{16}$N$_3$O$_2$ [M+H$^+$]: 234.1237, found: 234.1234.

Ethyl 2-(5,6-difluoro-1H-benzo[d][1,2,3]triazol-1-yl)acetate (5c)
Isolated in 63% yield (30.4 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (dd, $J = 9.0, 7.1$ Hz, 1H), 7.30 (dd, $J = 8.6, 6.6$ Hz, 1H), 5.39 (s, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.05, 150.67 (dd, $J = 524.7, 16.7$ Hz), 150.64 (dd, $J = 22.3, 16.5$ Hz), 141.29 (d, $J = 9.7$ Hz), 129.47 (d, $J = 11.4$ Hz), 106.81 (dd, $J = 20.2, 1.7$ Hz), 97.16 (d, $J = 23.7$ Hz), 62.72, 49.47, 14.17. HRMS (ESI) calcd. for C$_{10}$H$_{10}$F$_2$N$_3$O$_2$ [M+H$^+$]: 242.0736, found: 242.0735.

**Ethyl 2-(5,6-dichloro-1H-benzo[d][1,2,3]triazol-1-yl)acetate (5d)**

Isolated in 82% yield (44.8 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (s, 1H), 7.64 (s, 1H), 5.37 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.89, 144.96, 133.18, 132.44, 129.11, 121.07, 110.85, 62.68, 49.29, 14.08. HRMS (ESI) calcd. for C$_{10}$H$_{10}$Cl$_2$N$_3$O$_2$ [M+H$^+$]: 274.0145, found: 274.0144.

**Ethyl 2-(5-chloro-1H-benzo[d][1,2,3]triazol-1-yl)acetate (5e)**

Isolated in 31% yield (14.8 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 1.1$ Hz, 1H), 7.47 (d, $J = 8.8, 1.6$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 5.40 (s, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.17, 146.78, 132.21, 130.20, 128.97, 119.66, 110.46, 62.61, 49.38, 14.17. HRMS (ESI) calcd. for C$_{10}$H$_{11}$ClN$_3$O$_2$ [M+H$^+$]: 240.0534, found: 240.0534.

**Ethyl 2-(6-chloro-1H-benzo[d][1,2,3]triazol-1-yl)acetate (5e')**

Isolated in 38% yield (18.2 mg) as white solid.
1H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.95 (d, \( J = 8.8 \) Hz, 1H), 7.47 (d, \( J = 1.3 \) Hz, 1H), 7.31 (dd, \( J = 8.8, 1.7 \) Hz, 1H), 5.35 (s, 2H), 4.22 (q, \( J = 7.1 \) Hz, 2H), 1.24 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 166.16, 144.61, 134.41, 134.03, 125.39, 121.08, 109.36, 62.52, 49.12, 14.08. HRMS (ESI) calcd. for C\textsubscript{10}H\textsubscript{11}ClN\textsubscript{3}O\textsubscript{2}[M+H\textsuperscript{+}]: 240.0534, found: 240.0534.

Methyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)acetate (5f)

Isolated in 74% yield (28.3 mg) as yellow solid.

1H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.04 (d, \( J = 8.4 \) Hz, 1H), 7.50 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 5.40 (s, 2H), 3.74 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 166.92, 146.01, 133.39, 127.99, 124.18, 120.15, 109.27, 52.99, 48.89. HRMS (ESI) calcd. for C\textsubscript{9}H\textsubscript{10}N\textsubscript{3}O\textsubscript{2}[M+H\textsuperscript{+}]: 192.0768, found: 192.0764.

1-(1H-Benzo[d][1,2,3]triazol-1-yl)propan-2-one (5g)

Isolated in 20% yield (7.0 mg) as yellow solid.

1H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.09 (d, \( J = 8.3 \) Hz, 1H), 7.55 – 7.48 (m, 1H), 7.43 – 7.36 (m, 2H), 5.45 (s, 2H), 2.22 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 200.04, 146.09, 133.53, 128.16, 124.34, 120.34, 109.19, 56.92, 27.23. HRMS (ESI) calcd. for C\textsubscript{19}H\textsubscript{10}N\textsubscript{3}O\textsubscript{2}[M+H\textsuperscript{+}]: 176.0818, found: 176.0813.

Ethyl 2-(1H-benzo[d][1,2,3]triazol-1-yl)propanoate (5h)

Isolated in 79% yield (34.6 mg) as yellow liquid.

1H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.09 (d, \( J = 8.4 \) Hz, 1H), 7.58 – 7.46 (m, 2H), 7.42 – 7.36 (m, 1H), 5.71 (q, \( J = 7.4 \) Hz, 1H), 4.21 (q, \( J = 7.1 \) Hz, 2H), 2.03 (d, \( J = 7.4 \) Hz, 3H), 1.20 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 169.31, 146.44, 132.61, 127.67, 124.17, 120.37, 110.08, 62.38, 57.42, 16.83, 14.12. HRMS (ESI) calcd. for C\textsubscript{11}H\textsubscript{14}N\textsubscript{3}O\textsubscript{2}[M+H\textsuperscript{+}]: 220.1081, found: 220.1076.
**Ethyl-4-(1H-benzo[d][1,2,3]triazol-1-yl)but-2-enoate (5i)**

Isolated in 35% yield (16.2 mg) as yellow liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 – 8.06 (m, 1H), 7.56 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H), 7.12 (dt, $J = 15.7$, 5.2 Hz, 1H), 5.75 (dt, $J = 15.7$, 1.8 Hz, 1H), 5.46 (dd, $J = 5.2$, 1.8 Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.33, 146.24, 139.83, 132.95, 127.99, 124.40, 124.35, 120.42, 109.30, 61.00, 48.67, 14.23. HRMS (ESI) calcd. for C$_{12}$H$_{14}$N$_3$O$_2$ [M+H$^+$]: 232.1081, found: 232.1080.

**1-Benzyl-1H-benzo[d][1,2,3]triazole (5j)**

Isolated in 84% yield (35.1 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 – 8.06 (m, 1H), 7.44 – 7.27 (m, 8H), 5.86 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.46, 134.87, 132.93, 129.15, 128.62, 127.72, 127.55, 124.08, 120.22, 109.86, 52.42. HRMS (ESI) calcd. for C$_{13}$H$_{12}$N$_3$ [M+H$^+$]: 210.1026, found: 210.1022.

**1-(2-Methylbenzyl)-1H-benzo[d][1,2,3]triazole (5k)**

Isolated in 82% yield (36.6 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.29 (m, 2H), 7.28 – 7.12 (m, 4H), 7.04 (d, $J = 7.6$ Hz, 1H), 5.83 (s, 2H), 2.33 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.32, 136.61, 133.06, 132.65, 131.01, 128.74, 128.57, 127.40, 126.48, 126.93, 120.10, 109.93, 50.84, 19.33. HRMS (ESI) calcd. for C$_{14}$H$_{14}$N$_3$ [M+H$^+$]: 224.1182, found: 224.1180.

**1-(4-Nitrobenzyl)-1H-benzo[d][1,2,3]triazole (5l)**

Isolated in 84% yield (35.1 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.29 (m, 2H), 7.28 – 7.12 (m, 4H), 7.04 (d, $J = 7.6$ Hz, 1H), 5.83 (s, 2H), 2.33 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.32, 136.61, 133.06, 132.65, 131.01, 128.74, 128.57, 127.40, 126.48, 126.93, 120.10, 109.93, 50.84, 19.33. HRMS (ESI) calcd. for C$_{14}$H$_{14}$N$_3$ [M+H$^+$]: 224.1182, found: 224.1180.
Isolated in 92% yield (46.8 mg) as yellow solid

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, $J = 8.6$ Hz, 2H), 8.09 (d, $J = 8.2$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.43 – 7.35 (m, 4H), 5.97 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.97, 146.34, 141.95, 132.77, 128.33, 128.07, 124.41, 124.31, 120.40, 109.19, 51.17. HRMS (ESI) calcd. for C$_{13}$H$_{11}$N$_3$O$_2$ [M+H$^+$]: 255.0877, found: 255.0878.

**Benzo[e][1,2,4]triazin-3-yl(2-((4-methoxyphenyl)ethynyl)phenyl)methanone (6)**

Isolated in 90% yield (65.7 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.48 (d, $J = 8.4$ Hz, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 8.05 – 7.94 (m, 2H), 7.92 – 7.84 (m, 1H), 7.63 – 7.49 (m, 3H), 6.67 (d, $J = 8.7$ Hz, 2H), 6.51 (d, $J = 8.7$ Hz, 2H), 3.70 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.17, 159.71, 158.74, 147.46, 140.69, 138.71, 136.18, 133.14, 132.64, 132.61, 132.37, 130.41, 129.73, 129.68, 128.45, 124.30, 113.84, 113.69, 97.07, 86.67, 55.35. HRMS (ESI) calcd. for C$_{23}$H$_{16}$N$_3$O$_2$ [M+H$^+$]: 366.1237, found: 366.1239.

**11-(4-Methoxyphenyl)-6H-indeno[2,1-b]quinolin-6-one (7)**

Isolated in 75% yield (50.6 mg) as white solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J = 8.1$ Hz, 1H), 7.81 (s, 1H), 7.68 (t, $J = 7.1$ Hz, 1H), 7.57 (d, $J = 7.9$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.39 – 7.28 (m, 4H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.71 – 6.60 (m, 1H), 3.97 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.75, 160.26, 154.16, 148.60, 143.44, 141.86, 135.92, 134.71, 131.94, 131.34, 130.35, 130.19, 130.00, 129.52, 129.23, 127.02, 126.75, 124.91, 124.09, 114.95, 55.59. HRMS (ESI) calcd. for C$_{23}$H$_{16}$NO$_2$ [M+H$^+$]: 338.1176, found: 338.1177.
7. Spectra of new compounds

3a
5f