

# Supplementary Information

## Efficient Synthesis of Functionalized 1,2,3-Triazoles by Catalyst-Free 1,3-Dipolar Cycloaddition of Nitroalkenes with Sodium Azide

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### Experimental

#### General methods

All commercially available reagents and solvents were obtained from commercial providers and used without further purification. Reactions were monitored by TLC using silica gel 60 UV254 Macherey-Nagel pre-coated silica gel plates; detection was by means of a UV lamp. Column chromatography was performed using silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. Organic layers were dried over anhydrous MgSO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> prior to evaporation on a rotary evaporator. <sup>1</sup>H NMR spectra were recorded at 400 MHz, and <sup>13</sup>C NMR spectra were recorded at 100 MHz (Bruker Avance). Chemical shifts ( $\delta$ ) are reported in ppm downfield from CDCl<sub>3</sub> ( $\delta$  7.26 ppm) for <sup>1</sup>H NMR and relative to the central CDCl<sub>3</sub> resonance ( $\delta$  77.0 ppm) for <sup>13</sup>C NMR spectroscopy. Coupling constants (*J*) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ<sup>DECA</sup> ion trap mass spectrometer. Triazoles **2a**, **2c**, **2e**, **2f** and **2g** are known compounds.<sup>1</sup> Triazoles **2b**, **2d** and **2h-j** are new compounds and their physical and spectral properties are reported below.

#### A typical procedure for synthesis of **2a-2e**

To the solution of the nitroalkenes **1** (1 mmol) in DMSO (2 mL) was added sodium azide (2 mmol). The mixture was then heated at 80 °C until the starting material was totally consumed as indicated by TLC. After cooling, water was added and the resulting precipitate was filtered, washed with excess of water, and dried to give the desired triazole, which was recrystallized. When no precipitate was observed, the triazole was isolated after extraction with ethylacetate.

Further purification was done by column chromatography using ethylacetate/petroleum ether as eluent.

#### Chromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (**2a**)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.03 (d, 1H, *J* 7.7 Hz), 7.64 (dd, 1H, *J* 11.4, 4.2 Hz), 7.53 (d, 1H, *J* 8.3 Hz), 7.47 (t, 1H, *J* 7.5 Hz).

#### 8-Fluorochromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (**2b**)

Solid, mp 315 °C (dec.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.75 (m, 1H), 7.56 (m, 1H), 7.47 (m, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  164.7, 162.3, 159.5, 153.8, 124.7, 124.0, 123.7, 114.5, 114.3; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 856, 1009, 1140, 1472, 1523, 1642, 1744, 3215; ESI-HRMS: calc. for C<sub>9</sub>H<sub>4</sub>FN<sub>3</sub>O<sub>2</sub>+Na 228.0181, found 228.0178.

#### 8-Chlorochromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (**2c**)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.07 (d, 1H, *J* 2.5 Hz), 7.56 (dd, 1H, *J* 8.8, 2.3 Hz), 7.37 (d, 1H, *J* 8.8 Hz).

#### 8-Bromochromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (**2d**)

Solid, mp 336 °C (dec.). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.98 (d, 1H, *J* 2.3 Hz), 7.63 (dd, 1H, *J* 8.9, 2.4 Hz), 7.53 (d, 1H, *J* 8.9 Hz), 2.46 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  154.7, 151.3, 131.5, 129.2, 123.1, 119.8, 113.9; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 848, 1002, 1131, 1452, 1513, 1612, 1726, 3218; ESI-HRMS: calc. for C<sub>9</sub>H<sub>4</sub>BrN<sub>3</sub>O<sub>2</sub>+Na 287.9381, found 287.9377.

#### 7-Methoxychromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (**2e**)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, 1H, *J* 9.1 Hz), 6.81 (d, 2H, *J* 7.5 Hz), 3.76 (s, 3H).

#### A typical procedure for synthesis of **2f-j**

To the solution of the nitroalkenes **1** (1 mmol) in DMSO (2 mL) was added sodium azide (2 mmol). The mixture was

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then heated at 50 °C until the starting material was totally consumed as indicated by TLC. After cooling, water was added and the resulting precipitate was filtered, washed with excess of water, and dried to give the desired triazole, which was recrystallized. When no precipitate was observed, the triazole was isolated after extraction with ethylacetate. Further purification was done by column chromatography using ethylacetate/petroleum ether as eluent.

#### Ethyl 5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (**2f**)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.86-7.67 (m, 2H), 7.53-7.40 (m, 3H), 4.27 (m, 2H), 1.22 (t, 3H, *J* 7.1 Hz).

#### Ethyl 5-(4-chlorophenyl)-1*H*-1,2,3-triazole-4-carboxylate (**2g**)<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.80 (d, 2H, *J* 8.4 Hz), 7.55 (d, 2H, *J* 8.6 Hz), 4.28 (m, 2H), 1.25 (t, 3H, *J* 7.1 Hz).

#### Ethyl 5-(4-bromophenyl)-1*H*-1,2,3-triazole-4-carboxylate (**2h**)

Solid, mp 173-174 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.73 (d, 2H, *J* 8.1 Hz), 7.66 (d, 2H, *J* 8.3 Hz), 4.28 (dd, 2H, *J* 14.1, 7.0 Hz), 1.24 (t, 3H, *J* 7.1 Hz); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 161.3, 158.9, 152.8, 131.5, 123.2, 61.3, 14.3; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 846, 989, 1141, 1426, 1532, 1625, 1730, 2986; ESI-HRMS: calc. for C<sub>11</sub>H<sub>10</sub>BrN<sub>3</sub>O<sub>2</sub>+Na 294.9950, found 294.9943.

#### Ethyl 5-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (**2i**)

Solid, mp 297-298 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.66 (d, 2H, *J* 7.6 Hz), 7.29 (d, 2H, *J* 7.7 Hz), 4.28 (m, 2H), 2.36 (s, 3H), 1.25 (t, 3H, *J* 7.1 Hz); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 158.4, 156.0, 153.2, 129.3, 61.1, 21.3, 14.4; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 864, 991, 1145, 1473, 1536, 1616, 1749, 2997; ESI-HRMS: calc. for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>+Na 254.0902, found 254.0897.

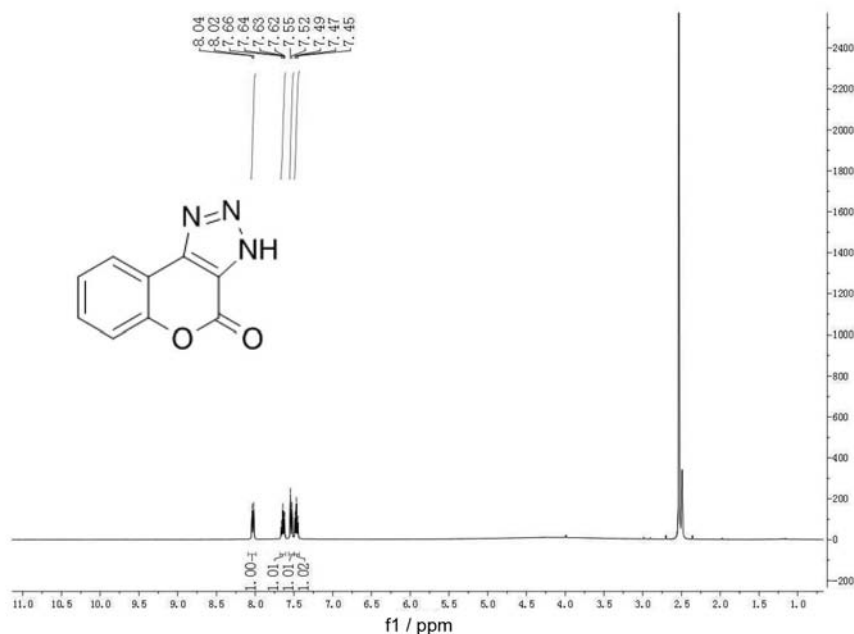
#### Ethyl 5-(furan-2-yl)-1*H*-1,2,3-triazole-4-carboxylate (**2j**)

Solid, mp 141-142 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.89 (s, 1H), 7.37 (s, 1H), 6.67 (dd, 1H, *J* 3.2, 1.7 Hz), 4.34 (m, 2H), 1.30 (t, 3H, *J* 7.1 Hz); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 160.9, 154.3, 144.9, 129.5, 113.6, 112.5, 110.1, 61.3, 14.5; IR (KBr)  $\nu_{\max}$ /cm<sup>-1</sup>: 851, 1007, 1125, 1453, 1526, 1609, 1750, 2996; ESI-HRMS: calc. for C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>O<sub>3</sub>+Na 230.0538, found 230.0531.

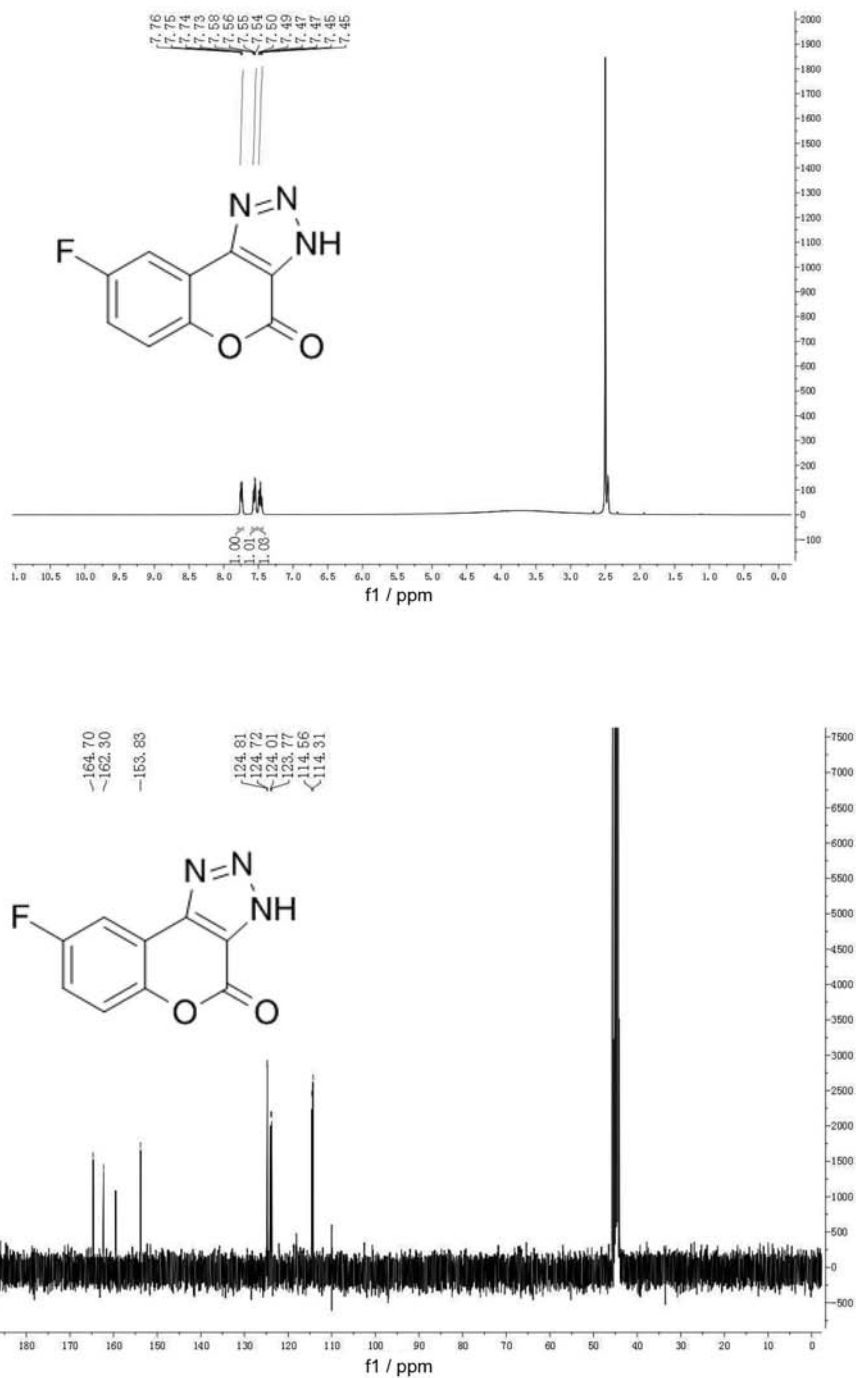
## Reference

- D'Ambrosio, G.; Fringuelli, F.; Pizzo, F.; Vaccaro, L.; *Green Chem.* **2005**, *7*, 874; Haryu, K.; Vahermo, M.; Mutikainen, I.; Yli-Kauhauloma, J.; *J. Comb. Chem.* **2003**, *5*, 826; Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Zunino, E.; Vaccaro, L.; *J. Org. Chem.* **2005**, *70*, 6526.

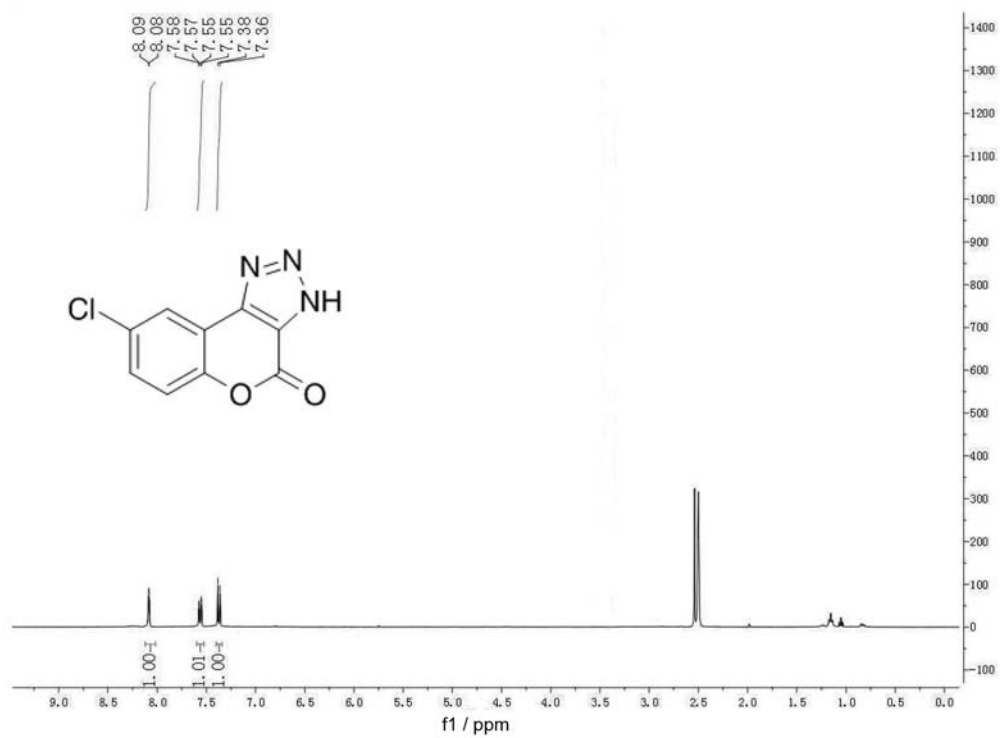
## NMR spectra



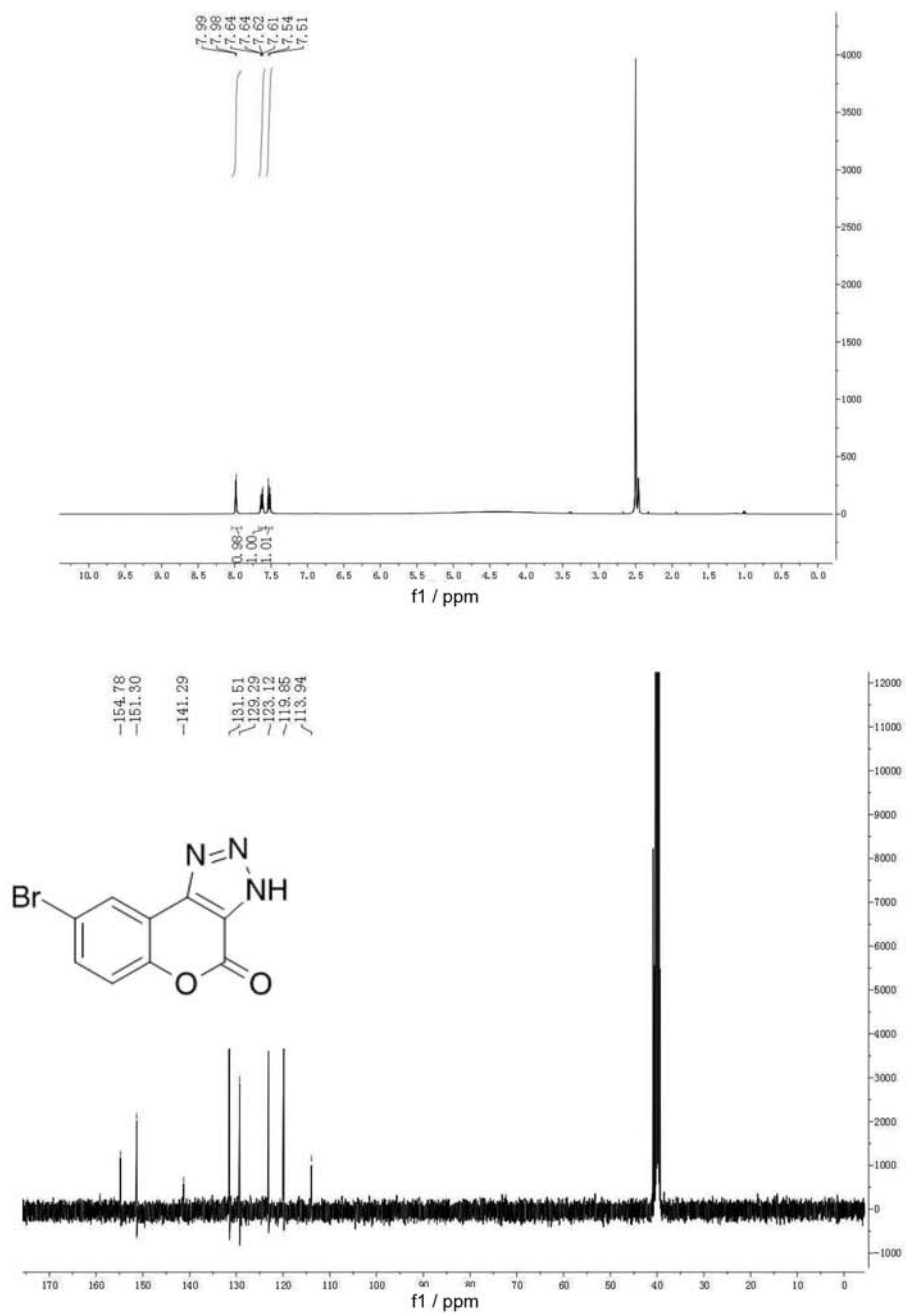
**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of chromeno[3,4-d][1,2,3] triazol-4(3H)-one (**2a**).



**Figure S2.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (400 MHz, DMSO-*d*<sub>6</sub>) of fluorochromeno[3,4-d][1,2,3]triazol-4(3H)-one (2b).



**Figure S3.** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>) of 8-chlorochromeno[3,4-d][1,2,3]triazol-4(3H)-one (2c).



**Figure S4.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (400 MHz,  $\text{DMSO}-d_6$ ) of 8-bromochromeno[3,4-d][1,2,3]triazol-4(3H)-one (**2d**).

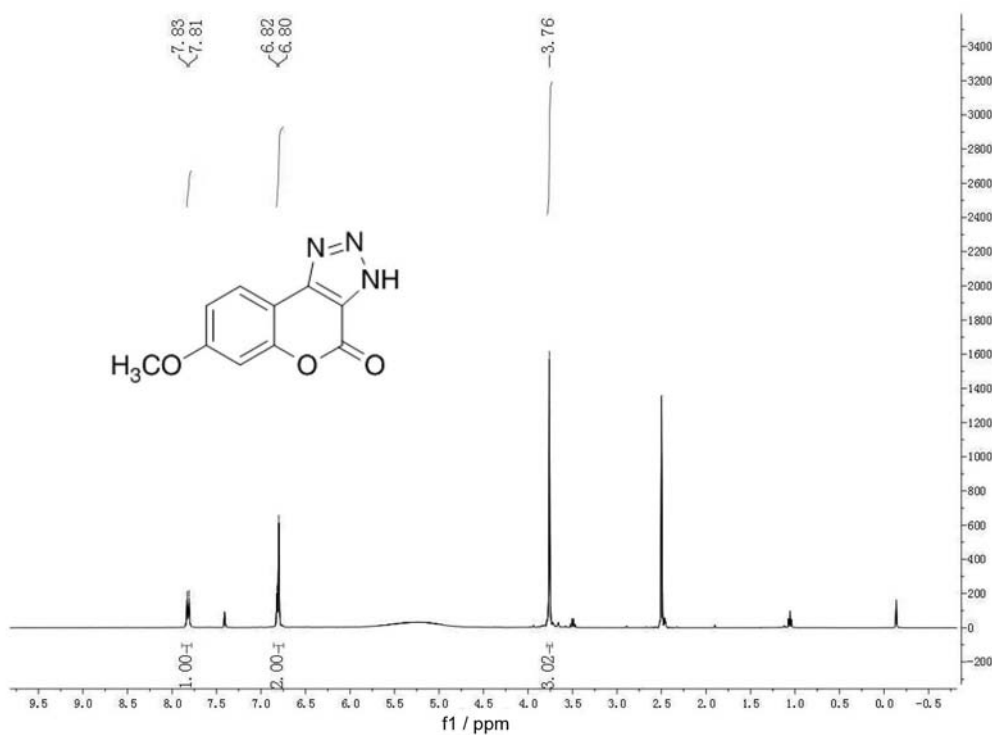


Figure S5. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>) of 7-methoxychromeno[3,4-d][1,2,3]triazol-4(3H)-one (2e).

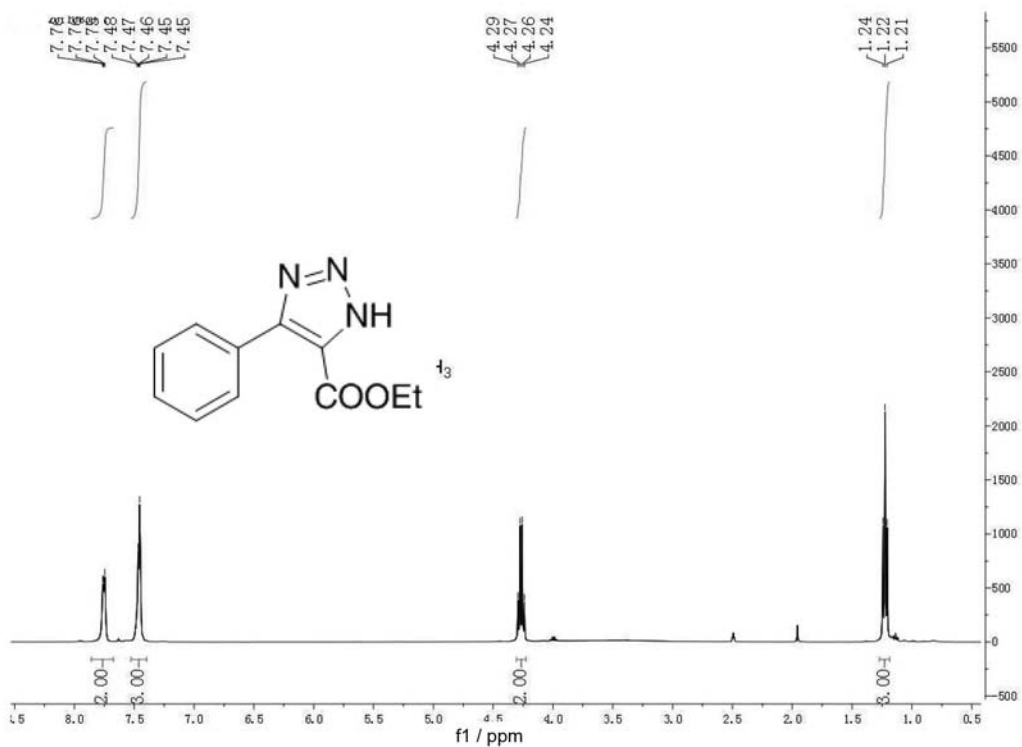
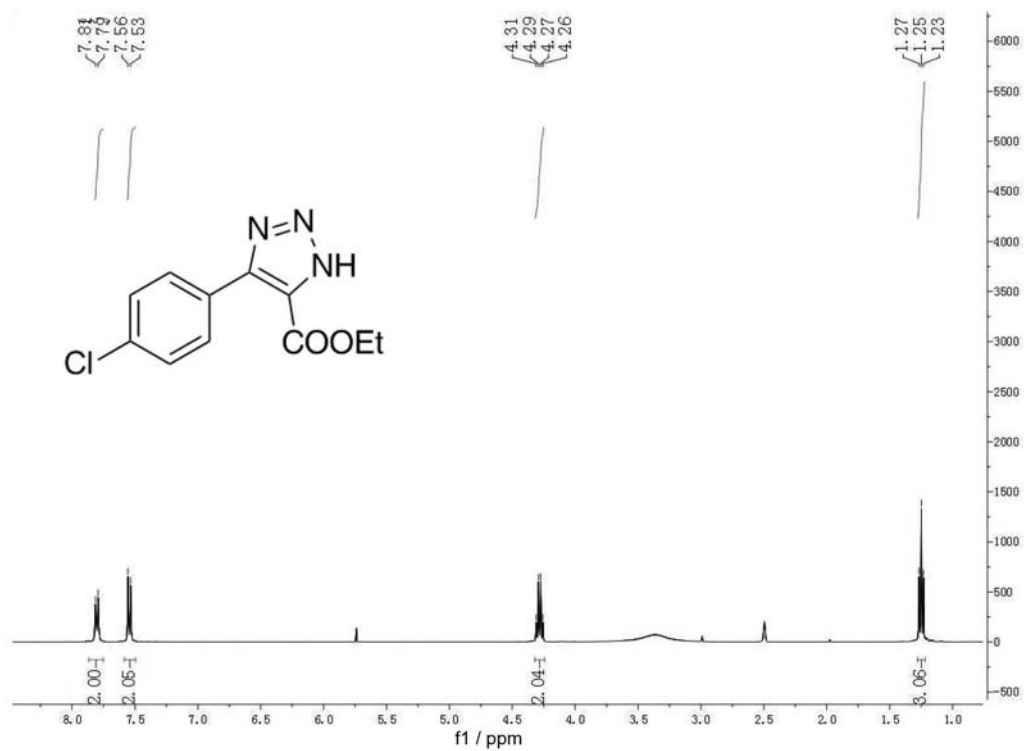
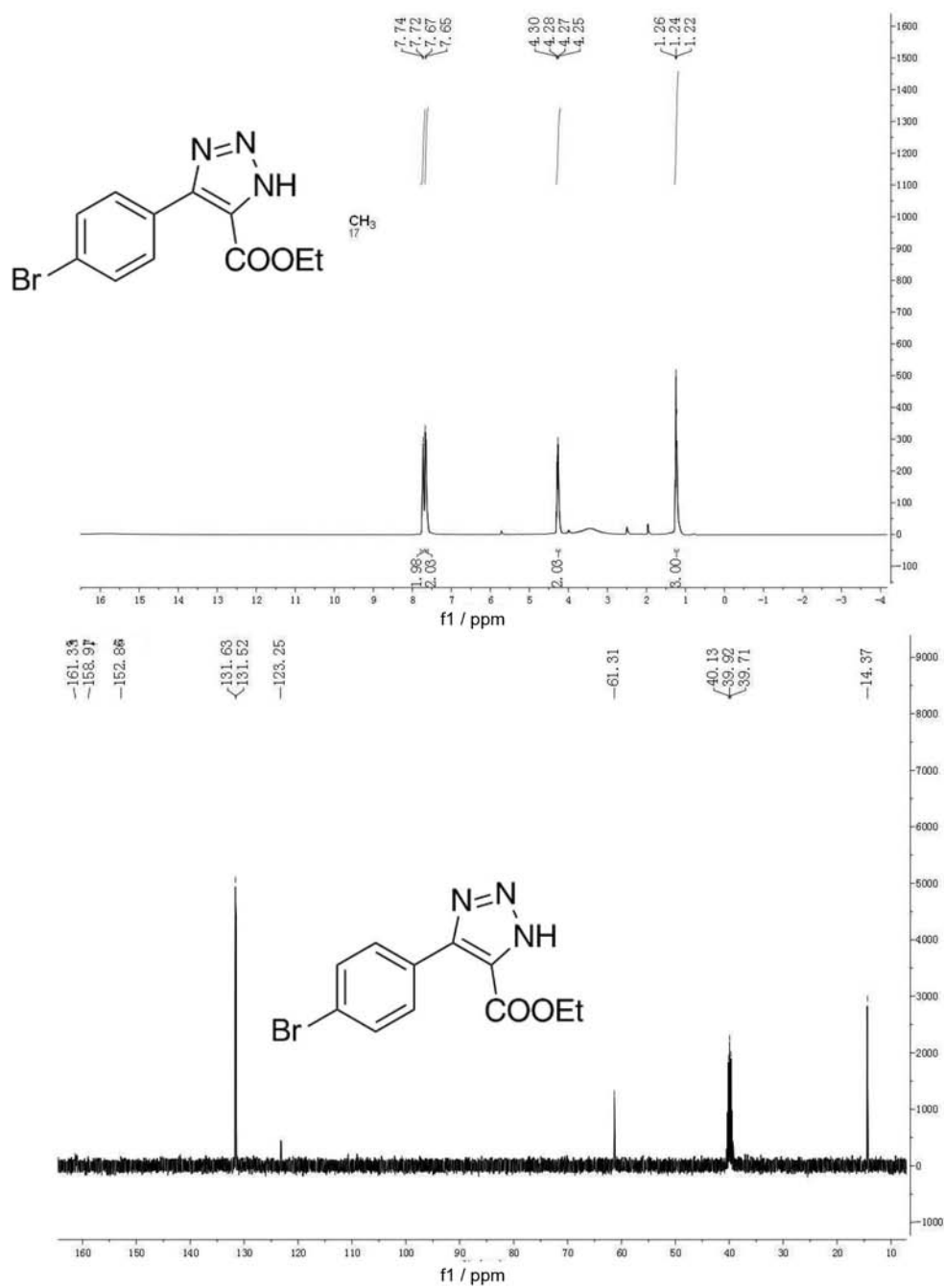


Figure S6. <sup>1</sup>H NMR spectrum (400 MHz, DMSO-d<sub>6</sub>) of ethyl 5-phenyl-1H-1,2,3-triazole-4-carboxylate (2f).

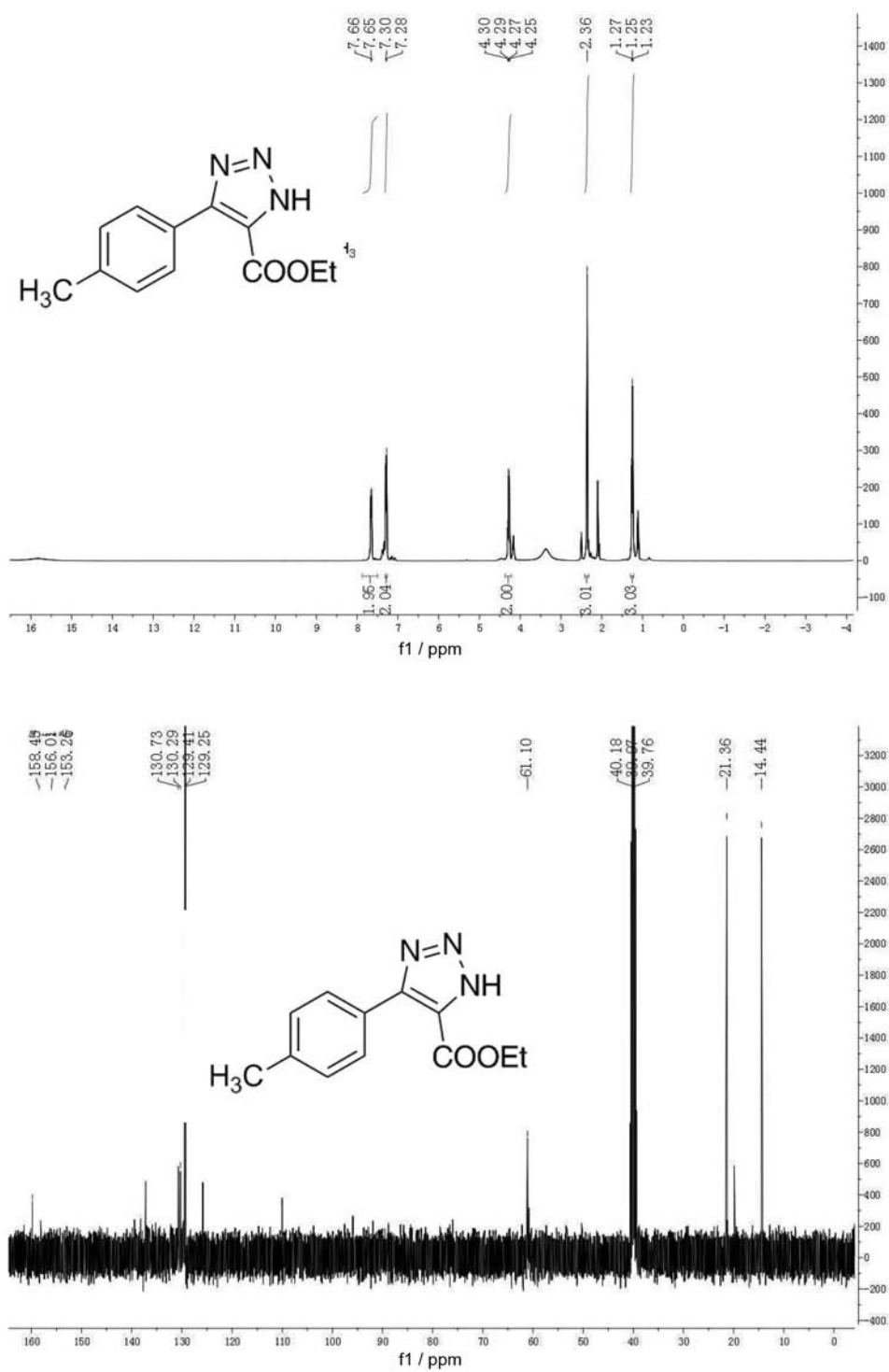


**Figure S7.** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of ethyl 5-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (**2g**).

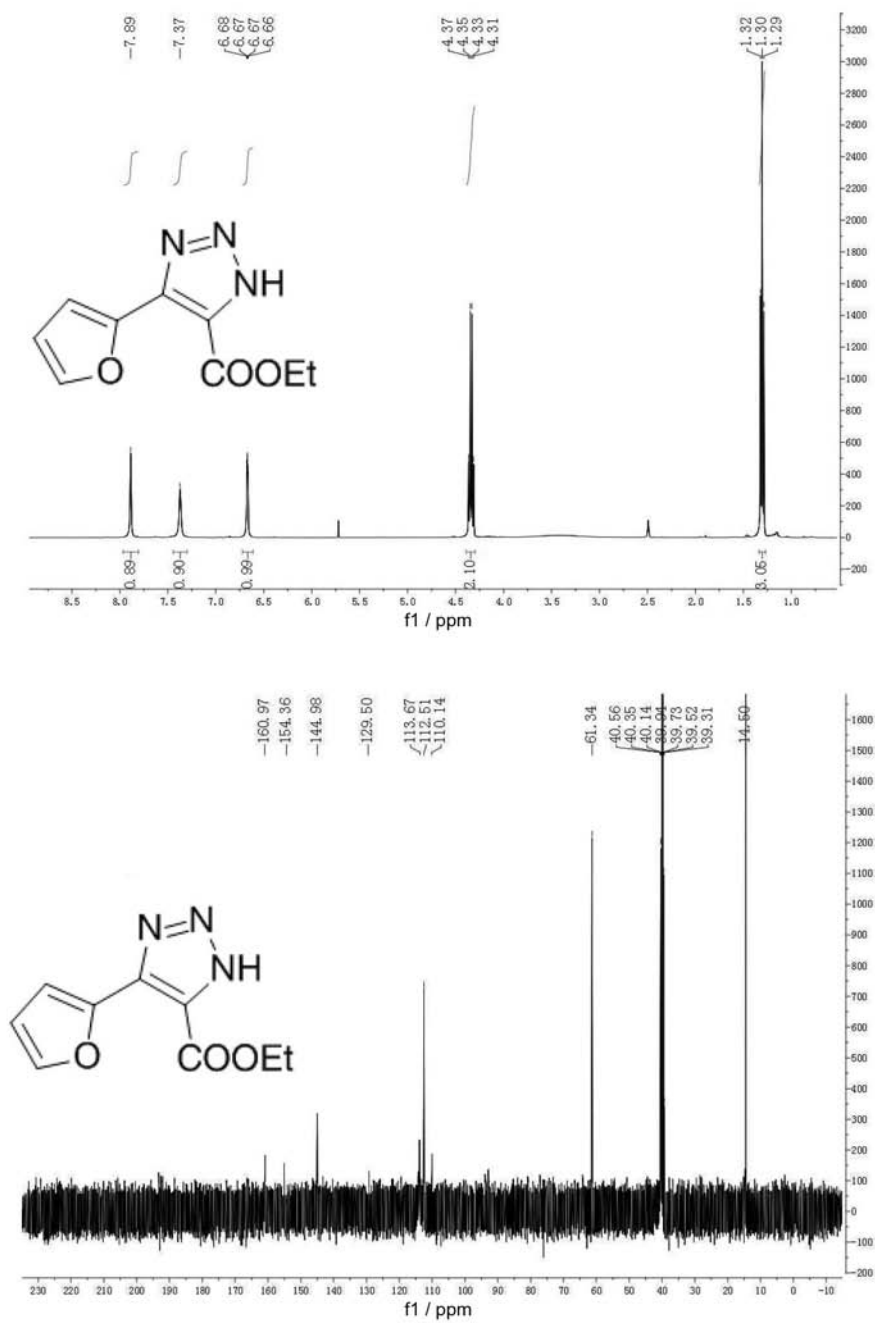


**Figure S8.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (400 MHz, DMSO-*d*<sub>6</sub>) of ethyl 5-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (**2h**).





**Figure S9.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (400 MHz, DMSO-*d*<sub>6</sub>) of ethyl 5-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (**2i**).



**Figure S10.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (400 MHz, DMSO-*d*<sub>6</sub>) of ethyl 5-(furan-2-yl)-1H-1,2,3-triazole-4-carboxylate (**2j**).