# *Article*

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

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Foi desenvolvido um protocolo simples e eficiente para a síntese de derivados de 1,2,3-triazol pela cicloadição 1,3-dipolar de nitroalquenos com azida de sódio, sem a necessidade de catalisador e sob condições brandas.

A simple and efficient protocol has been developed for the synthesis of 1,2,3-triazole derivatives by catalyst-free 1,3-dipolar cycloaddition of nitroalkenes with sodium azide under mild conditions.

**Keywords**: 1,2,3-triazoles, 1,3-dipolar cycloaddition, 3-nitrocoumarins, sodium azide, catalyst-free

## Introduction

Five-membered nitrogen heterocycles play an important role in biological systems. Among these, the 1,2,3-triazoles and their derivatives are of considerable interest as they possess a wide range of biological properties, such as anti-HIV,[1] anti-allergic,[2] anti-fungal,[3] anti-viral[4] and anti-microbial activity.[5] 1,2,3-Triazoles are important in pharmacological applications due to its stability toward light, moisture, oxygen, and metabolism in the body.[6] In addition, these moieties are widely applied as photosensitizers, dyes,[7] and commercially employed as anti-corrosive agents[8] in industry. Owing to the importance of these compounds, a variety of methods are known in the literature for the synthesis of pyrazoles, which include the thermal 1,3-dipolar cycloaddition of azide with various alkynes[9] and cycloaddition reactions of terminal alkynes with alkyl azides using Cu(I) as catalyst.[10] In addition, these molecules can also be prepared in one-pot procedure from alkynes with azides.[11] In fact, a straightforward approach to 1,2,3-triazoles is interesting and catalyst-free intermolecular 1,3-dipolar cycloaddition azides with electron-deficient alkenes to afford 1,2,3-triazoles, has been the subject of intensive research.[12] Recently, sodium azide has been used as a 1,3-dipole in 1,3-dipolar cycloaddition for the synthesis of 1,2,3-triazoles.[12] Considering the above reports and encouraged by the good results, we envisaged

that 1,3-dipolar cycloaddition would be possible between the α-carbonyl-β-aryl analogs of nitroethene with sodium azide, as outlined in Scheme 1. First, the reaction was happened via 1,3-dipolar cycloaddition of nitroalkenes with sodium ion as the key step. Then, elimination of the $NaNO_2$ and migration of hydrogen atom afford 1,2,3-triazoles.

## Results and Discussion

Coumarins are important heterocycles widely present in natural products exhibiting a broad range of biological and therapeutic activities and have been the subject of intensive research.[13] Recently, we have demonstrated the usefulness of the catalyst-free intermolecular 1,3-dipolar cycloaddition of 3-nitrocoumarins in the synthesis of functionalized pyrazoles with good yields.[14] We considered that the incorporation of a 1,2,3-triazole heterocyclic unit into 3-nitrocoumarins might provide 1,2,3-triazole derivatives that have important biological and pharmaceutical activities. Thus, we turned our attention to the possible synthesis of 1,2,3-triazoles using 3-nitrocoumarins **1** as dipolarophiles for the electron-poor 3-nitrocoumarins is a good dipolarophile with a good leaving group $NO_2$. The initial investigation started from the reaction between sodium azide and 3-nitrocoumarin **1a** (Table 1). It is known from the literature that the optimal medium for the reaction of sodium azide with nitroalkenes is DMSO.[13] Then we studied the reaction at different temperatures in DMSO, and found out that the best yield was obtained at 80 °C after
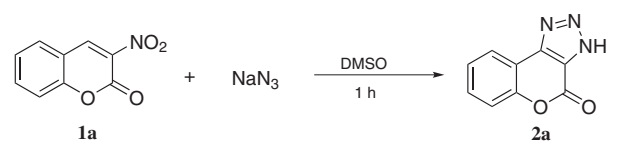
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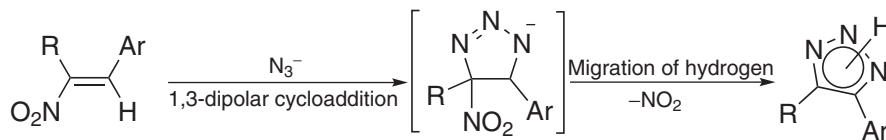
Scheme 1.

1 h (Table 1, entry 3). The structure was determined on the basis of $^1$H NMR in comparison with the literature data.[15]

**Table 1.** Catalyst-free 1,3-dipolar cycloaddition of nitroalkenes with sodium azide under different conditions[a]



| Entry | T / °C | Yield[b] / % |
|-------|--------|--------------|
| 1 | 25 | trace |
| 2 | 50 | 53 |
| 3 | 80 | 89 |

[a]Otherwise noted, reactions performed with 0.1 mmol of **1a**, 0.1 mmol of NaN$_3$ in 1 mL solvent. [b]Isolated yield.

Under the optimized conditions, these findings could be extended to the application of various other 3-nitrocoumarins **1a**-**1e**, and the 1,3-dipolar cycloaddition of 3-nitrocoumarins **1** to sodium azide proceeded smoothly to afford the chromeno[3,4-d][1,2,3]triazol-4(3$H$)-ones **2a**-**2e** as single regioisomers. The reaction's scope proved to be broad with respect to the 3-nitrocoumarins **1**. Good yields were obtained in the reactions of electron-withdrawing substituent on the aryl ring of 3-nitrocoumarins **1** with sodium azide (Table 2). In addition, an electron-donating substituent on the aryl ring of 3-nitrocoumarins **1** substrates tended to decrease their reactivity (Table 2, entry 5).

Having succeeded in synthesizing tricyclic 1,2,3-triazole derivatives, we then turned our attention to extend the scope of the 1,3-dipolar cycloaddition further. Acyclic α-carbethoxy-1-nitroalkenes **1f**-**1j** were utilized as

**Table 2.** Reaction scopes of 3-nitrocoumarins 1 with sodium azide in DMSO at 80 °C[a]
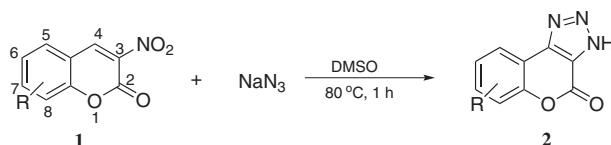


| Entry | R (**1**) | Product | **2** | Yield[b] / % |
|-------|-----------|---------|-------|--------------|
| 1 | H (**1a**) | | **2a** | 89 |
| 2 | 6-F (**1b**) | | **2b** | 82 |
| 3 | 6-Cl (**1c**) | | **2c** | 80 |
| 4 | 6-Br (**1d**) | | **2d** | 79 |
| 5 | 7-MeO (**1e**) | | **2e** | 66 |

[a]Otherwise noted, reactions performed with 1 mmol of **1** and 2 mmol of NaN$_3$ in 2 mL DMSO at 80 °C for 1 h. [b]Isolated yield.

**Table 3.** Reaction scopes of acyclic α-carbethoxy-1-nitroalkenes **1f**-**1j** with sodium azide in DMSO at 50 ºC[a]
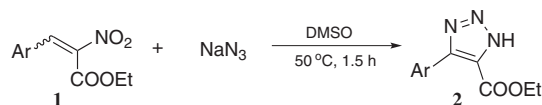


| Entry | R (**1**) | Product | **2** | Yield[b] / % |
|---|---|---|---|---|
| 1 | C$_6$H$_5$ (**1f**) | | **2f** | 76 |
| 2 | 4-ClC$_6$H$_4$ (**1g**) | | **2g** | 67 |
| 3 | 4-BrC$_6$H$_4$ (**1h**) | | **2h** | 62 |
| 4 | 4-MeC$_6$H$_4$ (**1i**) | | **2i** | 70 |
| 5 | 2-furyl (**1j**) | | **2j** | 79 |

[a]Otherwise noted, reactions performed with 1 mmol of **1**, 2 mmol of NaN$_3$ in 2 mL DMSO at 50 °C for 1.5 h. [b]Isolated yield.

dipolarophiles in the reaction with sodium azide. Unfortunately, very poor results were observed when the 1,3-dipolar cycloaddition of **1f**-**1j** with sodium azide was carried out at 80 ºC. To our delight, good yields were obtained when the reactions were carried out at 50 °C after 1 h (Table 3). Table 3 shows that α-carbethoxy-1-nitrostyrenes with electron-withdrawing or donating substituents provided the 1,2,3-triazole derivatives **2f**-**2i** in moderate-to-good yields of 62-76% (entries 2-4). The structures were also determined on the basis of ^{1}H NMR in comparison with the literature data.[15]

To explain the key step of the reaction between azidium ion and nitroalkenes, B3LYP/6-31g (d) calculations of stationary structures of azidium ion and nitroalkenes (**1a**-**j**) have been performed. It turned out that the global electrophilicity of azidium ion equals to 1.6 eV. At the same time it shows a strongly nucleophilic[16] characteristics (N = 7.97 eV). The nitrocoumarines (**1a**-**e**), on the other hand, show strongly electrophilic properties (global electrophilicity of (**1a**) = 3.28, (**1b**) = 3.55, (**1c**) = 3.62, (**1d**) = 3.62, (**1e**) = 2.94 eV). Their electrophilicity is therefore much higher than of the corresponding β-nitrostyrenes[17] and only slightly lower than of the corresponding β-cyano-β-nitrostyrenes.[18] In the case of a series of

β-carboethoxy-β-nitrostyrenes global electrophilicity is significantly lower (in particular: (**1i**) = 2.64, (**1f**) = 2.72, (**1g**) = 2.93, (**1h**) = 2.93 eV), but remain in the range typical for the strongly electrophilic dipolarophiles.[19] Notably, these reactions can be considered as polar1,3-dipolar cycloaddition (P-13DC).[20] Detailed analysis of the local electrophilicity indices on the reaction centers of nitroalkenes also revealed that the reaction was determined by the attack of nucleophilic atom of 1,3-dipole to β-position of nitroalkene, similarly as in the reactions of nitroethene with nitrones.[21]

## Conclusions

In conclusion, an efficient method for the synthesis of functionalized 1,2,3-triazoles by catalyst-free 1,3-dipolar cycloaddition of nitroalkenes with sodium azide has been investigated. The 1,3-dipolar cycloaddition can proceed smoothly under mild conditions and provides pure 1,2,3-triazole derivatives in good yields. The reaction's scope proved to be quite broad. Notably, we incorporated a 1,2,3-triazole heterocyclic unit into coumarins and provided substituted chromeno[3,4-*d*][1,2,3] triazol-4(1*H*)-one that might have important biological and pharmaceutical

activities in the future. This novel methodology should be of great interest for natural product synthesis for the mild reaction conditions.

## Experimental

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 $MgSO_4$ or $Na_2SO_4$ prior to evaporation on a rotary evaporator. $^1H$ NMR spectra were recorded at 400 MHz, and $^{13}C$ NMR spectra were recorded at 100 MHz (Bruker Avance). Chemical shifts ($\delta$) are reported in ppm downfield from $CDCl_3$ ($\delta$ 7.26 ppm) for $^1H$ NMR and relative to the central $CDCl_3$ resonance ($\delta$ 77.0 ppm) for $^{13}C$ NMR spectroscopy. Coupling constants ($J$) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ$^{DECA}$ ion trap mass spectrometer. 2-Aryl-1-carboethoxy-1-nitroethenes **1** were prepared according to reported procedure.[22] Triazoles **2a**, **2c**, **2e**, **2f** and **2g** are known compounds.[15] Triazoles **2b**, **2d** and **2h-j** are new compounds and their physical and spectral properties are reported in Supplementary Information section.

### General procedure for the synthesis of 1,2,3-triazoles **2** under the optimized conditions

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.

## Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

## Acknowledgments

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# *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 $MgSO_4$ or $Na_2SO_4$ prior to evaporation on a rotary evaporator. $^1H$ NMR spectra were recorded at 400 MHz, and $^{13}C$ NMR spectra were recorded at 100 MHz (Bruker Avance). Chemical shifts ($\delta$) are reported in ppm downfield from $CDCl_3$ ($\delta$ 7.26 ppm) for $^1H$ NMR and relative to the central $CDCl_3$ resonance ($\delta$ 77.0 ppm) for $^{13}C$ NMR spectroscopy. Coupling constants ($J$) are given in Hz. ESI-HRMS spectrometer was measured with a Finnigan LCQ$^{DECA}$ ion trap mass spectrometer. Triazoles **2a**, **2c**, **2e**, **2f** and **2g** are known compounds.[1] 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.

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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)**[1]
$^1H$ 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.). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.75 (m, 1H), 7.56 (m, 1H), 7.47 (m, 1H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 164.7, 162.3, 159.5, 153.8, 124.7, 124.0, 123.7, 114.5, 114.3; IR (KBr) $\nu_{max}$/cm$^{-1}$: 856, 1009, 1140, 1472, 1523, 1642, 1744, 3215; ESI-HRMS: calc. for $C_9H_4FN_3O_2$ +Na 228.0181, found 228.0178.

**8-Chlorochromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (2c)**[1]
$^1H$ 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.). $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 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); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 154.7, 151.3, 131.5, 129.2, 123.1, 119.8, 113.9; IR (KBr) $\nu_{max}$/cm$^{-1}$: 848, 1002, 1131, 1452, 1513, 1612, 1726, 3218; ESI-HRMS: calc. for $C_9H_4BrN_3O_2$+Na 287.9381, found 287.9377.

**7-Methoxychromeno[3,4-*d*][1,2,3]triazol-4(3*H*)-one (2e)**[1]
$^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 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

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**)[1]

$^1$H NMR (400 MHz, DMSO-$d_6$) 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**)[1]

$^1$H NMR (400 MHz, DMSO-$d_6$) 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. $^1$H NMR (400 MHz, DMSO-$d_6$) 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); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 161.3, 158.9, 152.8, 131.5, 123.2, 61.3, 14.3; IR (KBr) ν$_{max}$/cm$^{-1}$: 846, 989, 1141, 1426, 1532, 1625, 1730, 2986; ESI-HRMS: calc. for $C_{11}H_{10}BrN_3O_2$+Na 294.9950, found 294.9943.

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

Solid, mp 297-298 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) 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); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 158.4, 156.0, 153.2, 129.3, 61.1, 21.3, 14.4; IR (KBr) ν$_{max}$/cm$^{-1}$: 864, 991, 1145, 1473, 1536, 1616, 1749, 2997; ESI-HRMS: calc. for $C_{12}H_{13}N_3O_2$+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. $^1$H NMR (400 MHz, DMSO-$d_6$) 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); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 160.9, 154.3, 144.9, 129.5, 113.6, 112.5, 110.1, 61.3, 14.5; IR (KBr) ν$_{max}$/cm$^{-1}$: 851, 1007, 1125, 1453, 1526, 1609, 1750, 2996; ESI-HRMS: calc. for $C_9H_9N_3O_3$+Na 230.0538, found 230.0531.

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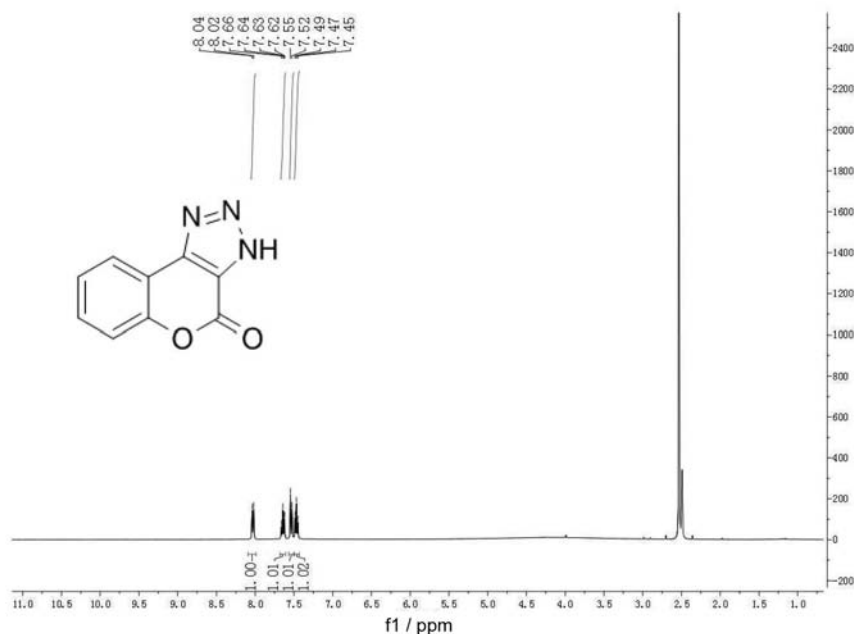
NMR spectra



**Figure S1.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of chromeno[3,4-d][1,2,3] triazol-4(3H)-one (**2a**).
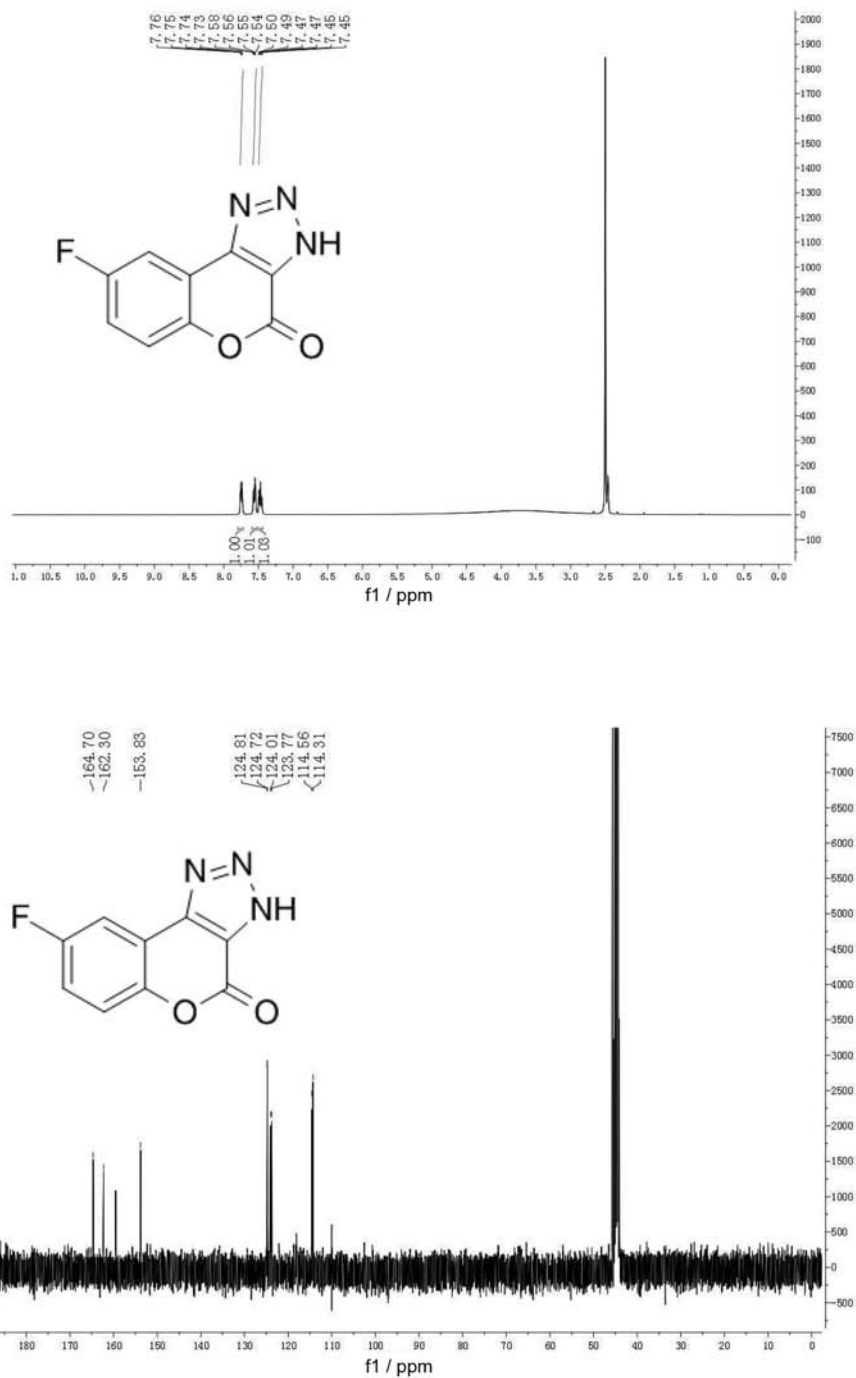
**Figure S2.** ¹H NMR and ¹³C NMR spectra (400 MHz, DMSO-$d_6$) of fluorochromeno[3,4-d][1,2,3]triazol-4(3H)-one (**2b**).
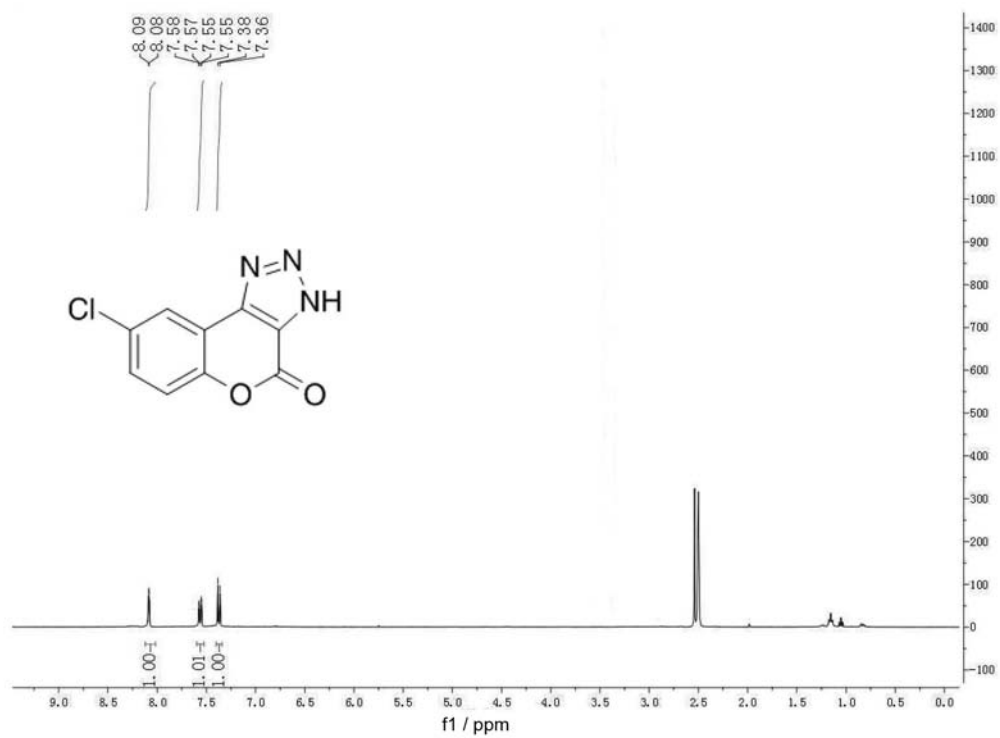
**Figure S3.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of 8-chlorochromeno[3,4-d][1,2,3]triazol-4(3H)-one (**2c**).
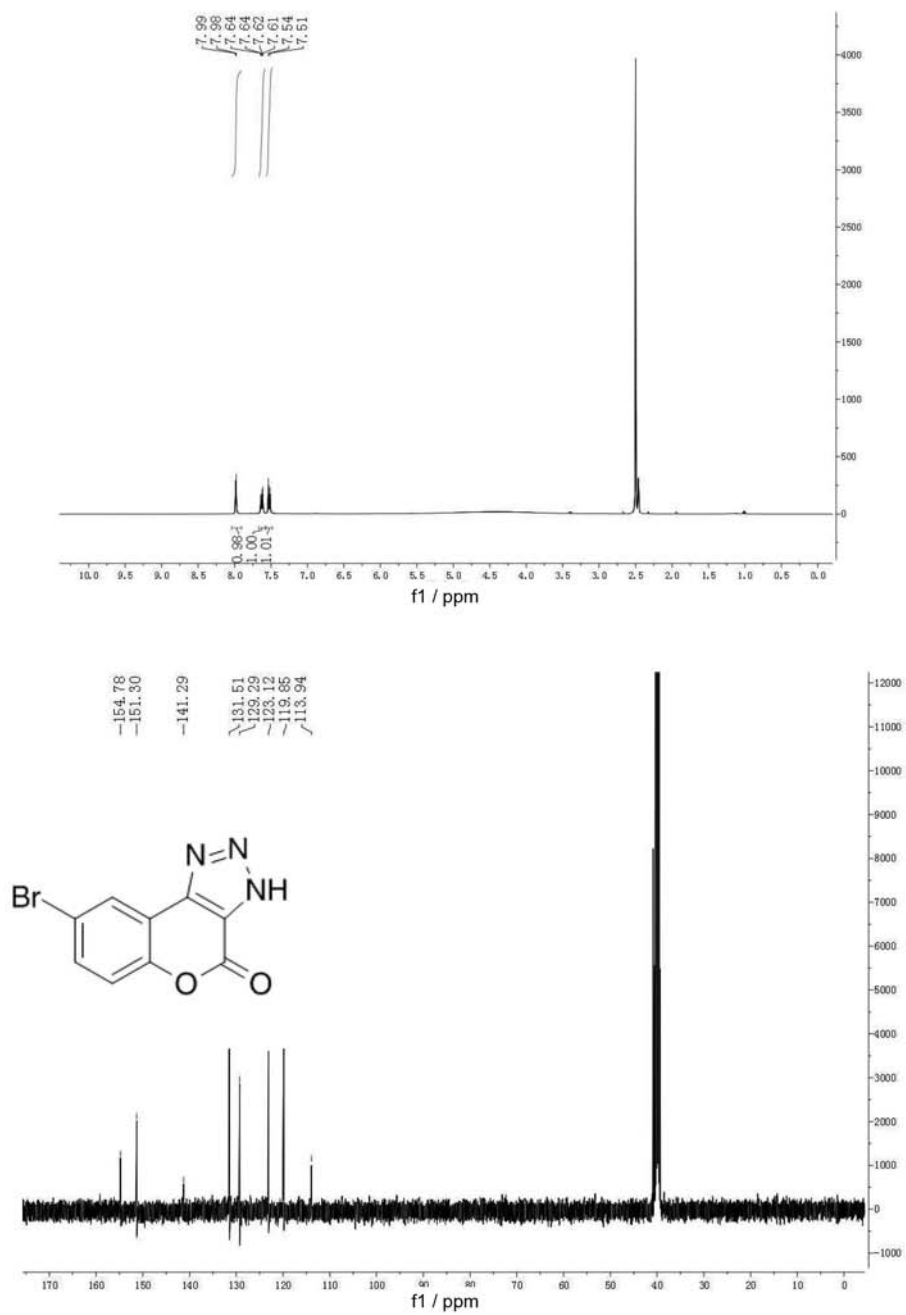
**Figure S4.** ^{1}H NMR and ^{13}C NMR spectra (400 MHz, DMSO-$d_6$) of 8-bromochromeno[3,4-d][1,2,3]triazol-4(3H)-one (**2d**).
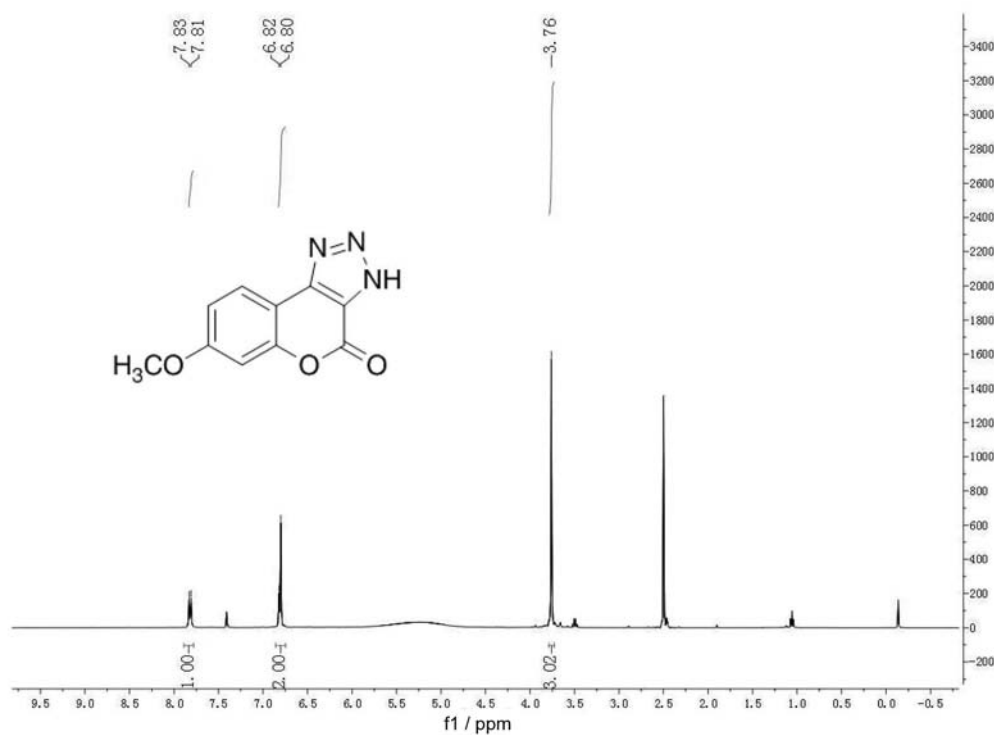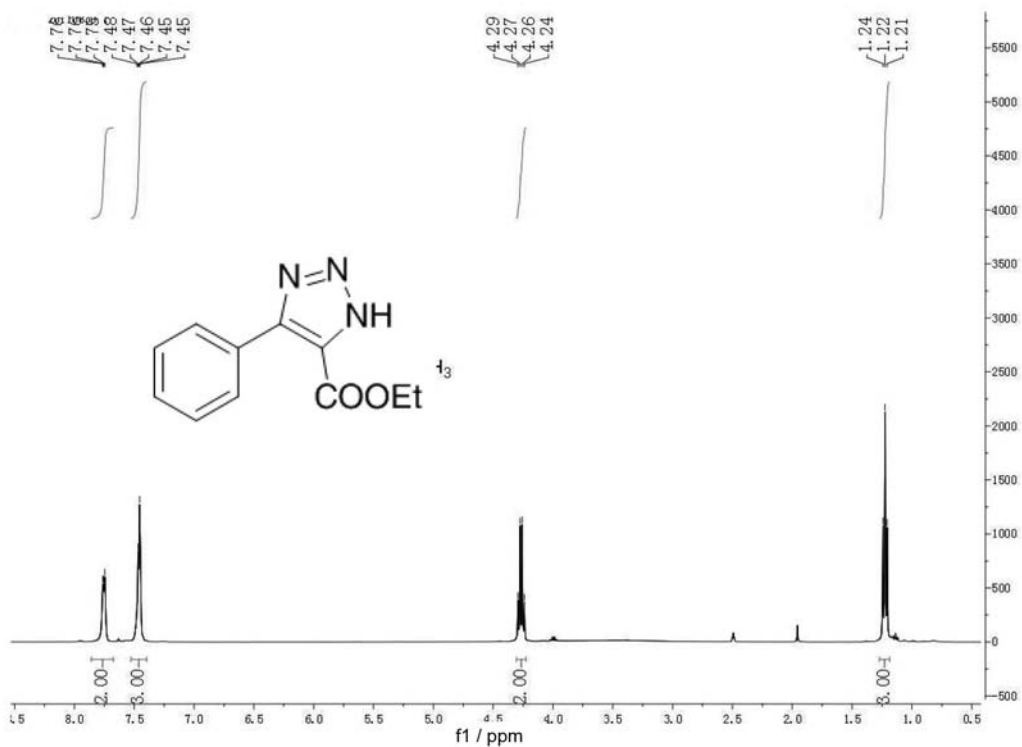
**Figure S5.** ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of 7-methoxychromeno[3,4-d][1,2,3]triazol-4(3H)-one (**2e**).



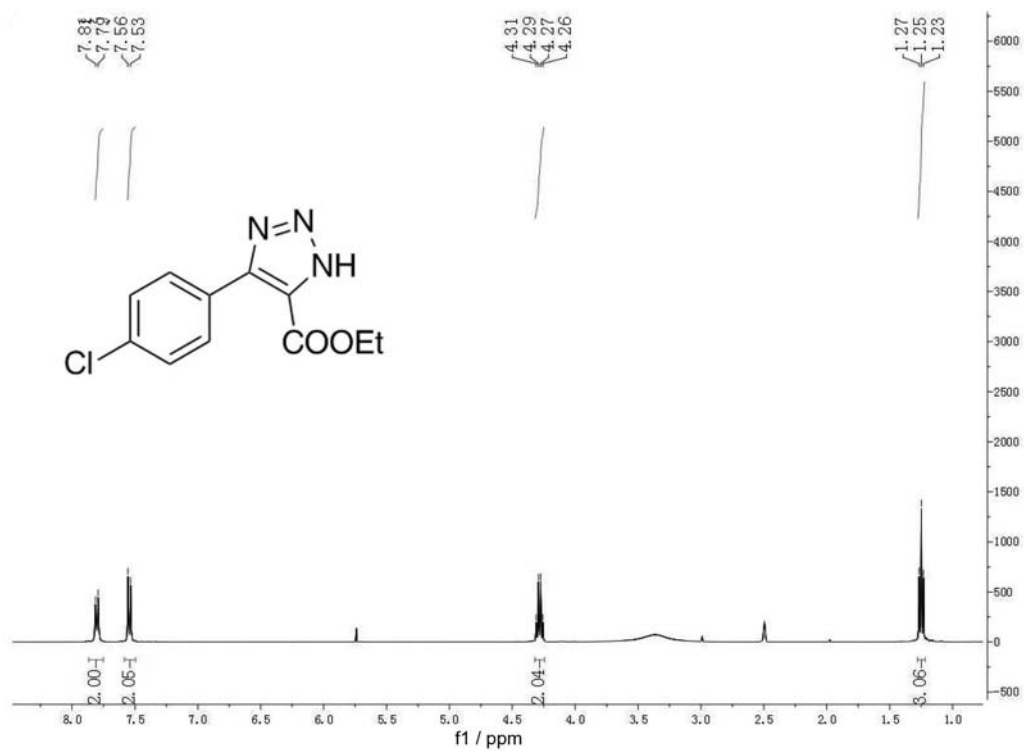**Figure S6.** ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of ethyl 5-phenyl-1H-1,2,3-triazole-4-carboxylate (**2f**).

**Figure S7.** $^1$H NMR spectrum (400 MHz, DMSO-$d_6$) of ethyl 5-(4-chlorophenyl)-1H-1,2,3-triazole-4-carboxylate (**2g**).
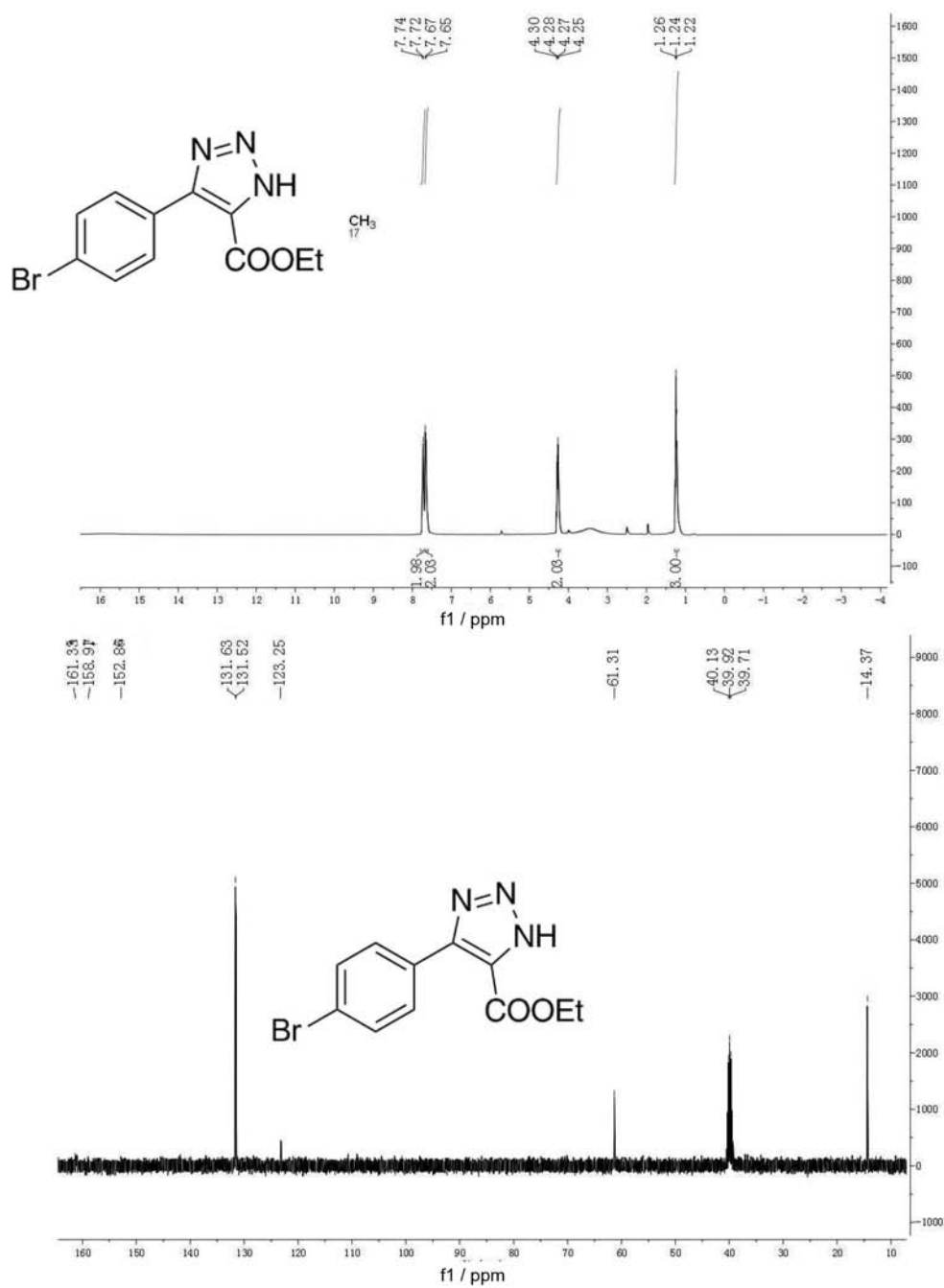
**Figure S8.** ¹H NMR and ¹³C NMR spectra (400 MHz, DMSO-*d*₆) of ethyl 5-(4-bromophenyl)-1H-1,2,3-triazole-4-carboxylate (**2h**).
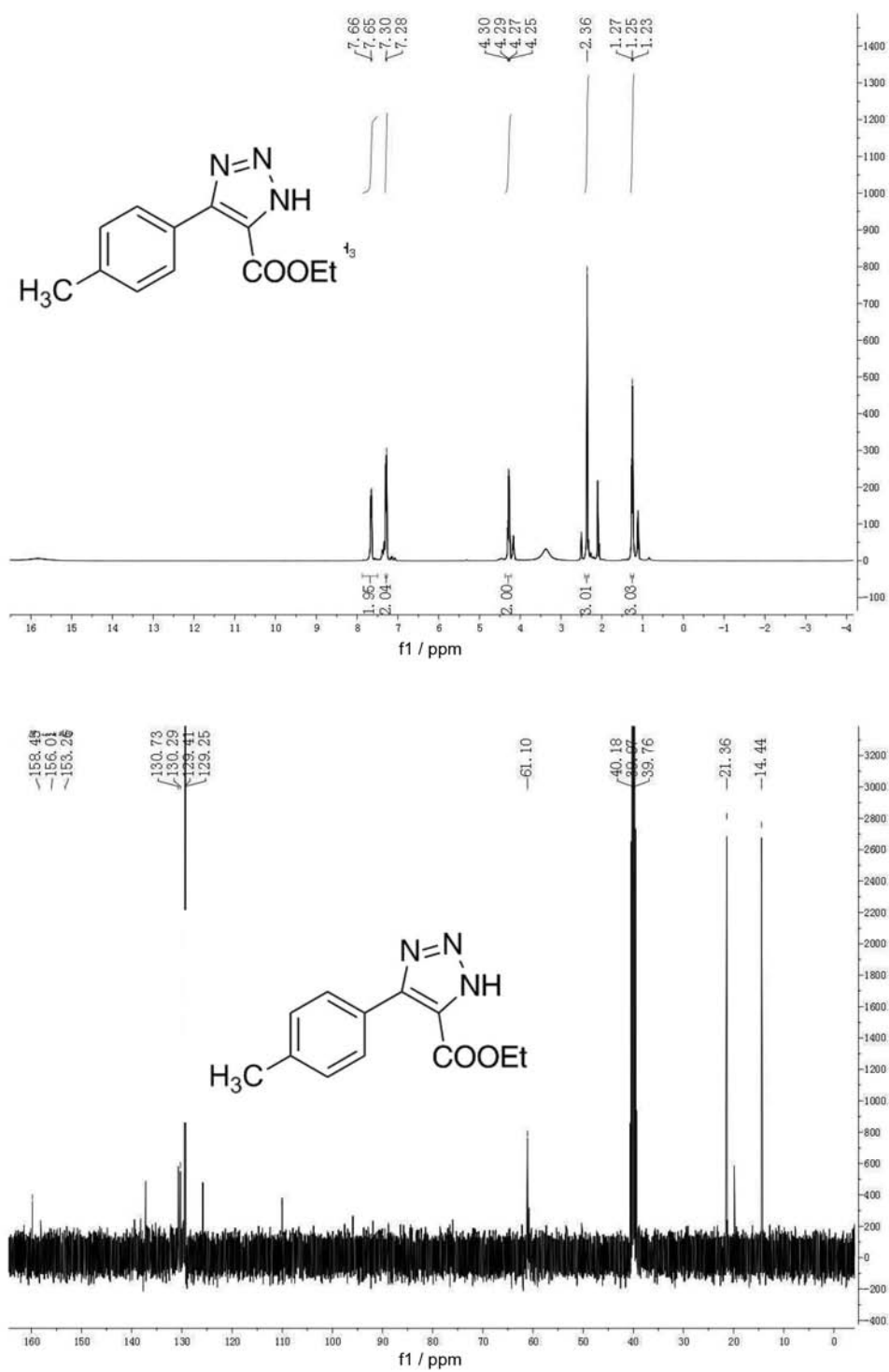
**Figure S9.** ^{1}H NMR and ^{13}C NMR spectra (400 MHz, DMSO-$d_6$) of ethyl 5-(p-tolyl)-1H-1,2,3-triazole-4-carboxylate (**2i**).
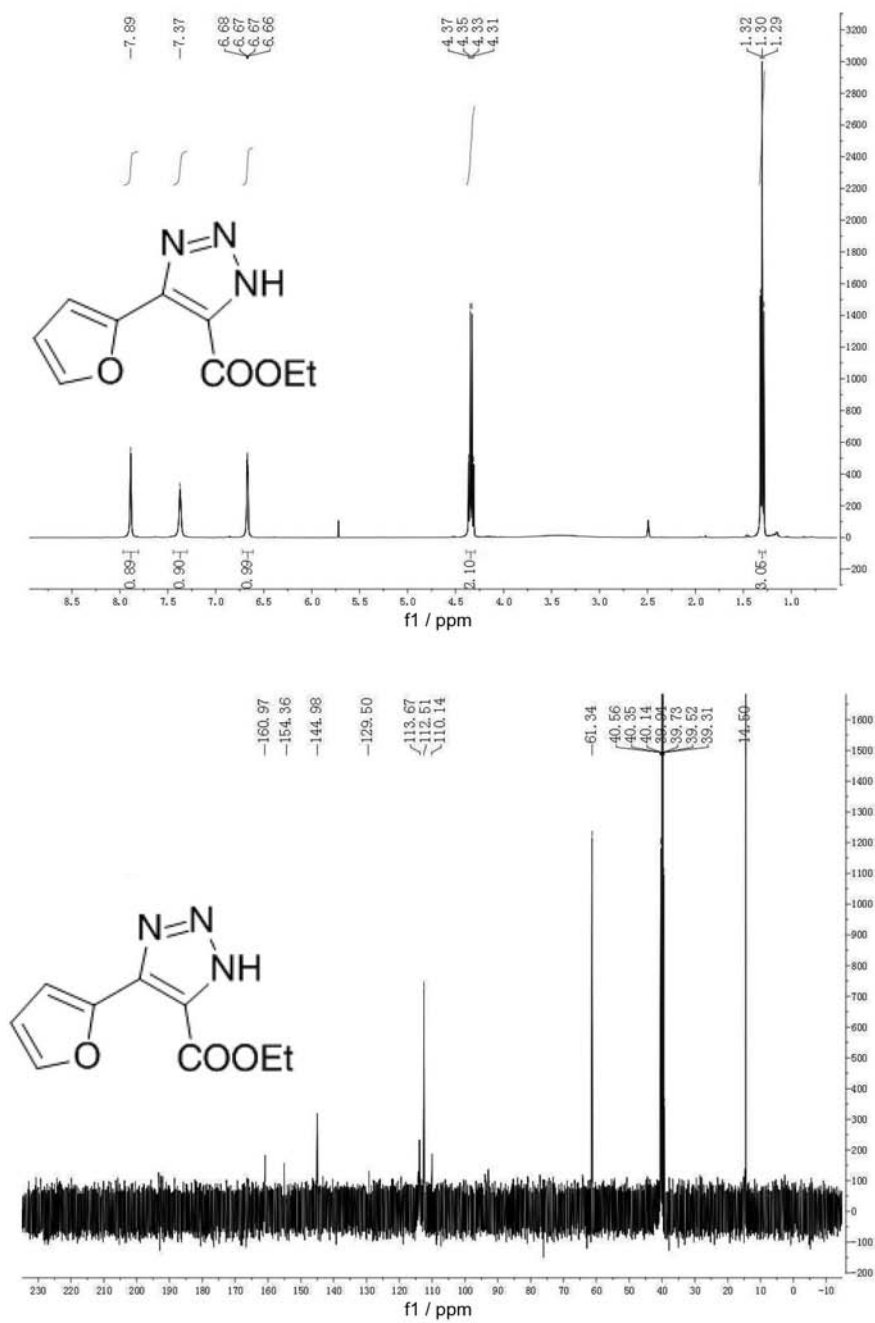
**Figure S10.** ¹H NMR and ¹³C NMR spectra (400 MHz, DMSO-$d_6$) of ethyl 5-(furan-2-yl)-1H-1,2,3-triazole-4-carboxylate (**2j**).