# A Mild Multi-Component Reaction for the Synthesis of 4,5-Disubstituted 1H-1,2,3-Triazoles from Phosphonium Salts, Aldehydes, and Sodium Azide 

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Abstract A mild and metal-free multi-component reaction to synthesize 4,5-disubstituted $1 H$-1,2,3-triazoles from phosphonium salts, aldehydes, and sodium azide is described. The process undergoes an organocatalyzed coupling of formyl group with phosphonium to form a key intermediate, olefinic phosphonium salt, which is followed by the [3+2] cycloaddition of the azide to the activated alkene. A series of representative 4,5-disubstituted 1 H -1,2,3-triazoles were prepared.

Key words phosphonium salt, triazole, organic catalyst, multicomponent reaction, cycloaddition

1,2,3-Triazoles are an important class of heterocyclic compounds, which have been widely used in organic synthesis, ${ }^{1}$ medicinal chemistry, ${ }^{2}$ and the development of new materials. ${ }^{3}$ Therefore, many methods have been developed to synthesize 1,2,3-triazoles till now. ${ }^{4}$ Among these developed approaches, most are for N -substituted 1,2,3-triazoles, and only a few are for N -unsubstituted 1,2,3-triazoles, which also have wide applications. ${ }^{5}$ Construction of 4,5-disubstituted 1 H -1,2,3-triazoles can be achieved via a tandem three-component reaction, involving the coupling of Julia reagent, ${ }^{5 \mathrm{~h}}$ nitroalkene, ${ }^{5 \mathrm{e}, \mathrm{j}, \mathrm{k}}$ or cyanocarbonyl compounds ${ }^{5 i}$ with aldehyde, followed by cycloaddition with sodium azide. In this paper, we report a mild method to synthesize 4,5 -disubstituted 1 H -1,2,3-triazoles by a multicomponent reaction from commercially inexpensive phosphonium salts, aldehydes, and sodium azide.

Phosphonium salts are usually deprotonated with a strong base to form phosphorus ylides, which have been studied intensively ever since the Wittig reaction became popular in the 1950s (Scheme 1) ${ }^{6 a, b}$ including new methods for the generation of phosphorus ylides, ${ }^{6 \mathrm{~b}, \mathrm{cj}}$ the synthesis of modified nucleosides, ${ }^{6 \mathrm{~d}}$ vinyl isocyanides, ${ }^{6 e}$ and macro-
cycles; ${ }^{6 f}$ by-product separation, ${ }^{68}$ and stereo- and regioselective olefination. ${ }^{6 h, i}$ We envisioned that phosphonium salt could also couple with aldehyde to form olefinic phosphonium salt, which is followed by a [3+2] cycloaddition with azide to produce a triazole ring as do acrylonitriles ${ }^{5 a}$ and $\alpha$ haloacrylates (Scheme 1).5s

## Wittig reaction:



This work:


Scheme 1 Reactions of phosphonium salts

Olefinic sulfur salt intermediates are formed via the coupling of sulfur salts with aldehydes in the presence of L-proline. ${ }^{7}$ Thus, our initial experiment was performed with (ethoxycarbonylmethyl)triphenylphosphonium bromide (1a), benzaldehyde (2a), and $\mathrm{NaN}_{3}$ catalyzed by L-proline. The mixture was stirred in DMSO solution at room temperature for 24 hours and the expected product, triazole 3a, was obtained in a $75 \%$ isolated yield. The Wittig product 4a was collected in an $11 \%$ yield (Table 1, entry 1 ). When the reaction was performed at $80^{\circ} \mathrm{C}$, the yield for the triazole product was reduced to $50 \%$, and the yield of the by-product, olefin, increased to $25 \%$ (entry 2). Thus, high temperature does not favor triazole formation. When DMSO was replaced with $\mathrm{EtOH}, \mathrm{MeOH}$, or MeCN as the solvent, all the reactions were negative (entries 3-5). In DMF solution, the yield of the main product, triazole, was moderate (51\%, en-

Table 1 Optimization of the Reaction Conditions ${ }^{\text {a }}$

|  <br> 1a | $+\mathrm{PhCHO}$2a |  |  <br> 3a |  <br> 4a |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| Entry | Solvent | Catalyst (mol\%) | Yield of 3a <br> (\%) ${ }^{\text {b }}$ | $\begin{aligned} & \text { Yield of } 4 \mathbf{a} \\ & (\%)^{b} \end{aligned}$ |
| 1 | DMSO | Proline (10) | 75 | 11 |
| $2^{\text {c }}$ | DMSO | Proline (10) | 50 | 25 |
| 3 | MeOH | Proline (10) | trace | trace |
| 4 | EtOH | Proline (10) | trace | trace |
| 5 | MeCN | Proline (10) | trace | trace |
| 6 | DMF | Proline (10) | 51 | 15 |
| 7 | THF | Proline (10) | trace | 61 |
| 8 | 1,4-Dioxane | Proline (10) | trace | 52 |
| 9 | $\mathrm{H}_{2} \mathrm{O}$ | Proline (10) | trace | trace |
| 10 | DMSO/ $\mathrm{H}_{2} \mathrm{O}$ (9:1) | Proline (10) | 32 | 40 |
| 11 | DMSO | Morpholine (10) | 71 | 16 |
| 12 | DMSO | Piperidine (10) | 68 | 18 |
| 13 | DMSO | Glycine (10) | 67 | 15 |
| 14 | DMSO | Serine (10) | 71 | 13 |
| 15 | DMSO | $\mathrm{K}_{2} \mathrm{CO}_{3}$ (100) | trace | 81 |
| 16 | DMSO | $\mathrm{K}_{2} \mathrm{CO}_{3}(10)$ | trace | 13 |
| 17 | DMSO | TsOH (20) | NR | NR |
| 18 | DMSO | - | NR | NR |

${ }^{\text {a }}$ Reagents and conditions: $\mathbf{1 a}(345 \mathrm{mg}, 0.8 \mathrm{mmol}), \mathrm{PhCHO}(\mathbf{2 a} ; 128 \mathrm{mg}$, $1.2 \mathrm{mmol}), \mathrm{NaN}_{3}(79 \mathrm{mg}, 1.2 \mathrm{mmol})$, catalyst, and solvent ( 5 mL ), r.t., 24 h . NR: No reaction.
${ }^{\mathrm{b}}$ Isolated yields.
c The reaction was performed at $80^{\circ} \mathrm{C}$ for 24 h .
try 6). In a weak polar solvent, tetrahydrofuran or 1,4-dioxane, only the olefin product was produced in a yield of $61 \%$ or $52 \%$, respectively, which is the Wittig reaction, and was probably attributable to the insolubility of $\mathrm{NaN}_{3}$ (entries 7 and 8). Neither triazole 3a nor olefin 4a was observed in the water solution (entry 9). However, in a solution of DMSO/ $\mathrm{H}_{2} \mathrm{O}(9: 1, \mathrm{v} / \mathrm{v})$, triazole 3a and olefin 4a were obtained in isolated yields of $32 \%$ and $40 \%$, respectively (entry 10 ).

The catalytic activities of both morpholine and piperidine were also examined and both proved to be effective in selectively producing the triazole product 3a in yields of $71 \%$ and $68 \%$, respectively (Table 1, entries 11 and 12 ). Other amino acids like glycine and serine were also examined and good yields were observed (entries 13 and 14). Notably, the amount of L-proline or amines used in this procedure was only $10 \mathrm{~mol} \%$ of the phosphonium salt, rather than the stoichiometric amount of a base that is usually involved in the Wittig reaction. ${ }^{8}$ Additionally, Wittig product 3a was
obtained in $81 \%$ and $13 \%$ yields and trace triazole product was observed when $\mathrm{K}_{2} \mathrm{CO}_{3}$ was used in $100 \mathrm{~mol} \%$ and 10 $\mathrm{mol} \%$, respectively (entries 15 and 16), indicating that strong bases promote the formation of the Wittig product. ${ }^{9}$ $p$-Toluenesulfonic acid was unsuitable for the formation of triazole or olefins (entry 17). In the control experiment, no product was formed in the absence of L-proline or amines (entry 18).

With the optimized conditions, the scope of aldehydes in this multistep reaction was screened (Scheme 2). The results indicated that electron-donating groups (Me, MeO, MeS , or $\mathrm{NMe}_{2}$ ) or weakly electron-withdrawing groups ( F , $\mathrm{Cl}, \mathrm{Br}$, or $\mathrm{CF}_{3}$ ) on the aromatic aldehydes favored the generation of the corresponding triazoles in yields of 63-81\% (compounds 3b-j). However, strong electron-withdrawing groups ( $\mathrm{CN}, \mathrm{NO}_{2}$, and $\mathrm{CO}_{2} \mathrm{Me}$ ) did not favor this tandem reaction (yields: 31-45\%, 31-n). 4,5-Disubstituted 1H-1,2,3triazole 3k containing a phenol hydroxyl group was formed in a much lower yield (28\%). Compared with thiophen-2-yl aldehyde, pyridine-3-yl aldehyde gave rise to a much lower yield (yield: $35 \%$ and $63 \%$ for compounds $\mathbf{3 o}$ and $\mathbf{3 p}$, respectively). Furthermore, butyraldehyde produced the corresponding triazole $\mathbf{3 q}$ in a $71 \%$ yield, similar to the results for aromatic aldehydes with an electron-donating group (compounds 3a-d).

Besides the (ethoxycarbonylmethyl)triphenylphosphonium bromide (1a) described above, phosphonium salts prepared by the quaternization of triphenylphosphine with bromomethyl ketone compounds were also examined under mild conditions (Scheme 3). The results indicated that the electron-withdrawing phenyl ketone produced $\alpha$-keto $1 H-1,2,3$-triazoles in lower yields ( $\mathbf{5 c}$ vs $\mathbf{5 a}$ and $\mathbf{5 b}$ ) than the cyclopropyl bromomethyl ketone. Under similar conditions, (cyanomethyl)triphenylphosphonium bromide showed good reactivity in the formation of a few corresponding 1 H -1,2,3-triazoles 5d-f. (Benzyl)triphenylphosphonium bromide failed to be transformed to the corresponding triazole product 5 g possibly because of the failure in the coupling of benzaldehyde with the phosphonium salt under these mild conditions. However, acylmethyl and cyanomethylphosphonium salts can generate 4,5-disubstituted 1 H -1,2,3-triazoles through their sequential coupling with aldehyde and $\mathrm{NaN}_{3}$ under these mild metal-free conditions.

To clarify the mechanism, LC-MS was used to monitor the reaction of (ethoxycarbonylmethyl)triphenylphosphonium bromide ( $\mathbf{1 a}$ ) with 4-methylthiobenzaldehyde, and $\mathrm{NaN}_{3}$ for triazole 3h. The mass spectrum (positive ESI) showed a peak at $m / z=263.1$, exactly matching the calculated value for the molecular weight of protonated triphenylphosphine $\left(\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{P}-\mathrm{H}^{+}, m / z=263.9\right) .{ }^{10}$ Moreover, in the absence of $\mathrm{NaN}_{3}$, a peak at $m / z=483.1$ is observed, which exactly matches the calculated value for the molecular weight of the olefinic triphenylphosphonium ion II $\left(\mathrm{C}_{30} \mathrm{H}_{28} \mathrm{O}_{2} \mathrm{SP}^{+}, m / z=483.1\right)$ (vide infra, Scheme 4). ${ }^{10}$ In the ${ }^{31} \mathrm{P}$ NMR spectra for the by-product, a strong signal at -5.41
ppm should also be assigned to triphenylphosphine. ${ }^{10}$ Triphenylphosphine oxide, however, is a well-known byproduct of the Wittig reaction. ${ }^{11}$ In addition, the possibility

> 1a
> 2
> $3 b-q$


Scheme 2 Triazoles generated from various aldehydes


Scheme 3 Triazoles generated from various phosphonium salts and aldehydes
of the addition of azides to electron-deficient olefins like 4a was examined by coupling ethyl cinnamate (4a) with sodium azide under similar conditions. A negative result was observed (Scheme 5), which indicates that 4a is not an intermediate for triazole product but a by-product (Table 1). Accordingly, a plausible pathway for the formation of $\mathrm{Ph}_{3} \mathrm{P}$ and the triazole product is described in Scheme 4. In the presence of L-proline and sodium azide, phosphonium salt I couples with protonated aldehyde to form the olefinic phosphorus salt II. ${ }^{12,13} \mathrm{~A}[3+2]$ cycloaddition between II and the azide anion generates the 4,5 -disubstituted triazole product, ${ }^{14}$ and triphenylphosphine ${ }^{15}$ is released via the aro-matization-promoted elimination.


Scheme 4 Proposed mechanism for sequentially coupling phosphonium salt with aldehyde and sodium azide


Scheme 5 No Reaction between 4a and sodium azide

In conclusion, a multi-component reaction to construct 4,5-disubstituted $1 \mathrm{H}-1,2,3$-triazoles by sequentially coupling phosphonium salts with aldehydes and azide has been developed. This method features mild and metal-free conditions. Starting from commercial and readily available reagents, it provides an easy access to diversely functionalized 4,5-disubstituted 1H-1,2,3-triazoles. Notably, the olefinic triphenylphosphonium salt was previously demonstrated to be generated via the coupling of phosphonium salts with aldehydes.

All reactions were performed under air. All reagents were used without further purification. Column chromatography was used for isolating the product and performed using 200-300 mesh silica gel with the proper solvent system according to TLC analysis using $\mathrm{KMnO}_{4}$ stain and UV light to visualize the reaction components. NMR spectra
were recorded in $\mathrm{CDCl}_{3}, \mathrm{CD}_{3} \mathrm{OD}$ or DMSO- $d_{6}$, with proton and carbon resonances at 300 or 400 and 75 MHz , respectively, and are referenced to the residual solvent signal at $\delta=7.28\left(\mathrm{CDCl}_{3}\right), 4.89\left(\mathrm{CD}_{3} \mathrm{OD}\right)$, $2.50 \mathrm{ppm}\left(\mathrm{DMSO}-d_{6}\right)$ for ${ }^{1} \mathrm{H}$ and $\delta=77.27\left(\mathrm{CDCl}_{3}\right), 47.82\left(\mathrm{CD}_{3} \mathrm{OD}\right)$, $40.17 \mathrm{ppm}\left(\mathrm{DMSO}-d_{6}\right)$ for ${ }^{13} \mathrm{C}$. Data for ${ }^{1} \mathrm{H}$ are reported as follows: chemical shift ( $\delta \mathrm{ppm}$ ), multiplicity (standard abbreviations), coupling constant, and integration. Data for ${ }^{13} \mathrm{C}$ NMR are reported in terms of chemical shift. MS and HRMS were measured in ESI mode, and the mass analysis mode of the HRMS was TOF.

4,5-Disubstituted 1,2,3-Triazoles; Ethyl 4-Phenyl-1H-1,2,3-tri-azole-5-carboxylate (3a); ${ }^{16}$

## Typical Procedure

To a reaction flask equipped with a magnetic stir bar was added (ethoxycarbonylmethyl)triphenylphosphonium bromide (1a; 345 mg , 0.8 mmol ), benzaldehyde (2a; $128 \mathrm{mg}, 1.2 \mathrm{mmol}$ ), $\mathrm{NaN}_{3}(79 \mathrm{mg}, 1.2$ mmol ), and L-proline ( $9 \mathrm{mg}, 0.08 \mathrm{mmol}$ ). The mixture was dissolved in DMSO ( 5 mL ) and stirred at r.t. for 24 h . After completion of the reaction, the mixture was poured into ice-water and extracted with $\mathrm{EtOAc}(4 \times 20 \mathrm{~mL})$. The combined organic layers were dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$, and the solvent was concentrated in vacuo. The residue was isolated by chromatography on silica gel with EtOAc/PE (1:2) as eluent to afford the product 3a; yield: $131 \mathrm{mg}(75 \%)$; white solid; $\mathrm{mp} 92-94{ }^{\circ} \mathrm{C}$; $R_{f}=0.55$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.87-7.85\left(\mathrm{~m}, 2 \mathrm{H}_{\text {arom }}\right), 7.48-7.47(\mathrm{~m}, 3$ $\left.\mathrm{H}_{\text {arom }}\right), 4.45\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.38(\mathrm{t}, 3 \mathrm{H}, J=7.1 \mathrm{~Hz}$, $\mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.1,146.2,134.1,129.7,129.3,128.3$, 127.7, 61.7, 14.1.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 218.0924$; found: 218.0916.

## Ethyl 4-(p-Tolyl)-1H-1,2,3-triazole-5-carboxylate (3b) ${ }^{5 \mathrm{~d}}$

Eluent: EtOAc/PE (1:2); yield: 185 mg (79\%); white solid; mp 129$130{ }^{\circ} \mathrm{C} ; R_{f}=0.55(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.73\left(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.16(\mathrm{~d}, J=$ $\left.8.1 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.40\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 2.40\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{ArCH}_{3}\right)$, $1.33\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.3,146.2,140.1,134.1,129.3,129.3$, 124.8, 61.9, 21.6, 14.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 232.1081$; found: 232.1074.

Ethyl 4-(4-Methoxyphenyl)-1H-1,2,3-triazole-5-carboxylate (3c) ${ }^{17}$ Eluent: EtOAc/PE (1:2); yield: 133 mg (78\%); white solid; mp 122$125{ }^{\circ} \mathrm{C} ; R_{f}=0.54(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.77\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 6.92(\mathrm{~d}, \mathrm{~J}=$ $\left.8.9 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.36\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.82\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right)$, $1.30\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.6,160.88,145.3,133.7,130.9$, 119.7, 113.9, 61.7, 55.5, 14.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 248.1030$; found: 248.1027.

Ethyl 4-(2-Methoxyphenyl)-1H-1,2,3-triazole-5-carboxylate (3d) ${ }^{17}$
Eluent: EtOAc/PE (1:2); yield: 129 mg (75\%); white solid; mp 123$125^{\circ} \mathrm{C} ; R_{f}=0.53(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.62-7.28\left(\mathrm{~m}, 2 \mathrm{H}_{\text {arom }}\right), 7.28-6.82(\mathrm{~m}$, $\left.2 \mathrm{H}_{\text {arom }}\right), 4.23\left(\mathrm{q}, \mathrm{J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.77\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 1.18(\mathrm{t}$, $\left.J=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=161.6,157.3,139.9,135.7,131.4$, 131.0, 120.2, 116.3, 110.9, 60.9, 54.9, 13.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}$: 248.1030; found: 248.1026.

Ethyl 4-(4-Bromophenyl)-1H-1,2,3-triazole-5-carboxylate (3e) ${ }^{\text {5d }}$
Eluent: EtOAc/PE (1:2); yield: 169 mg (80\%); white solid; mp 169$171{ }^{\circ} \mathrm{C} ; R_{f}=0.56(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( 300 MHz, DMSO- $d_{6}$ ): $\delta=7.74\left(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right.$ ), $7.68(\mathrm{~d}$, $\left.J=8.6 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.28\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.25(\mathrm{t}, J=7.1 \mathrm{~Hz}$, $3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( 75 MHz, DMSO- $d_{6}$ ): $\delta=161.4,145.1,131.9,131.8,131.5$, 128.4, 123.4, 61.5, 14.6.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{BrN}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}$: 296.0029, 298.0009; found: 296.0029, 298.0006.

Ethyl 4-(4-Fluorophenyl)-1H-1,2,3-triazole-5-carboxylate (3f) ${ }^{\text {5e }}$
Eluent: EtOAc/PE (1:2); yield: 126 mg (65\%); colorless oil; $R_{f}=0.55$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H} \mathrm{NMR} \mathrm{( } 300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.91\left(\mathrm{dd}, J_{1}=5.6 \mathrm{~Hz}, J_{2}=8.4 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right)$, $7.15-7.2\left(\mathrm{~m}, 2 \mathrm{H}_{\text {arom }} \mathrm{H}\right), 4.45\left(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.40(\mathrm{t}, J=$ $\left.7.2 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=165.4(\mathrm{~d}, \mathrm{~J}=248 \mathrm{~Hz}), 161.2,146.8$, $134.2,131.6(\mathrm{~d}, J=7.4 \mathrm{~Hz}), 124.5,115.8(\mathrm{~d}, J=22.6 \mathrm{~Hz}), 62.2,14.4$.
HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{FN}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 236.0830$; found: 236.0826.

## Ethyl 4-(3-Chlorophenyl)-1H-1,2,3-triazole-5-carboxylate (3g) ${ }^{\text {5e }}$

Eluent: EtOAc/PE (1:2); yield: 153 mg (63\%); white solid; mp 101$103^{\circ} \mathrm{C} ; R_{f}=0.56$ (PE/EtOAC $1: 1$ ).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.90\left(\mathrm{~s}, 1 \mathrm{H}_{\text {arom }}\right), 7.81-7.70\left(\mathrm{~m}, 1 \mathrm{H}_{\text {arom }}\right)$, $7.54-7.42\left(\mathrm{~m}, 2 \mathrm{H}_{\text {arom }}\right), 4.39\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.36(\mathrm{t}, J=7.1$ $\left.\mathrm{Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=160.8,144.7,133.9,130.6,129.7$, 129.2, 129.1, 127.6, 127.5, 61.3, 13.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{ClN}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 252.0534$; found: 252.0524.

## Ethyl 4-[4-(Methylthio)phenyl]-1H-1,2,3-triazole-5-carboxylate

 (3h)Eluent: EtOAc/PE (1:2); yield: 152 mg (81\%); white solid; mp 118$120^{\circ} \mathrm{C} ; R_{f}=0.51(\mathrm{PE} / E t O A c 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=7.78\left(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.29(\mathrm{~d}, J=$ $\left.8.4 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.40\left(\mathrm{q}, \mathrm{J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 2.51\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{SCH}_{3}\right)$, $1.33\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=161.3,141.3,129.7,129.7,125.8,124.3$, 124.1, 62.0, 15.5, 14.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}: 264.0801$; found: 264.0793.

Ethyl 4-[4-(Dimethylamino)phenyl]-1H-1,2,3-triazole-5-carboxylate (3i) ${ }^{18}$
Eluent: EtOAc/PE (2:3), yield: 183 mg (65\%); white solid; mp 124$126{ }^{\circ} \mathrm{C} ; R_{f}=0.43(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.68\left(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 6.83(\mathrm{~d}, J=$ $\left.8.9 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.38\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.04[\mathrm{~s}, 6 \mathrm{H}$, $\mathrm{N}\left(\mathrm{CH}_{3}\right)_{2}$ ], $1.37\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=161.6,151.8,143.8,130.0,128.7$, 113.7, 111.5, 60.9, 39.2, 13.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{13} \mathrm{H}_{16} \mathrm{~N}_{4} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}$: 261.1346; found: 261.1344.

Ethyl 4-[4-(Trifluoromethyl)phenyl]-1H-1,2,3-triazole-5-carboxylate ( $\mathbf{3 j})^{17}$
Eluent: EtOAc/PE (1:2); yield: 147 mg (78\%); white solid; mp 151$152{ }^{\circ} \mathrm{C} ; R_{f}=0.51$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=8.04\left(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.79(\mathrm{~d}, J=$ $\left.8.2 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.39\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.35(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3$ $\mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=160.8,145.1,132.9,130.7$, 129.8, 126.1, 124.9 ( $q, J=204 \mathrm{~Hz}$ ), 122.5, 61.4, 13.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{11} \mathrm{~F}_{3} \mathrm{~N}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 286.0798$; found: 286.0788.

Ethyl 4-(4-Hydroxyphenyl)-1H-1,2,3-triazole-5-carboxylate (3k) ${ }^{17}$ Eluent: EtOAc/PE (1:1); yield: 106 mg (28\%); white solid; mp 164$166{ }^{\circ} \mathrm{C} ; R_{f}=0.40(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta=7.64\left(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 6.90(\mathrm{~d}, J=$ $\left.8.7 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.36\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.35(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3$ $\mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR (75 MHz, CD ${ }_{3} \mathrm{OD}$ ): $\delta=161.4,159.1,144.0,130.7,125.5$, 118.0, 115.0, 61.0, 13.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 234.0873$; found: 234.0867.

Ethyl 4-[4-(Methoxycarbonyl)phenyl]-1H-1,2,3-triazole-5-carboxylate (31) ${ }^{17}$
Eluent: EtOAc/PE (1:2); yield: 107 mg (45\%); white solid; mp 108$110{ }^{\circ} \mathrm{C} ; R_{f}=0.50(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta=8.12\left(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.95(\mathrm{~d}, J=$ $\left.8.5 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.39\left(\mathrm{~d}, \mathrm{~J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.96\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right)$, $1.35\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=166.7,160.9,145.1,133.3,130.6$, 129.2, 129.1, 126.4, 61.4, 51.6, 13.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{13} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{4}[\mathrm{M}+\mathrm{H}]^{+}$: 276.0979; found: 276.0969.

Ethyl 4-(4-Cyanophenyl)-1H-1,2,3-triazole-5-carboxylate (3m) ${ }^{17}$
Eluent: EtOAc/PE (1:1), yield: 135 mg (38\%); white solid; mp 119$122{ }^{\circ} \mathrm{C} ; R_{f}=0.47(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(301 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta=8.01\left(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.79(\mathrm{~d}, J=$ $\left.8.4 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.34\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.31(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3$ $\mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=160.6,145.2,133.8,132.2,131.9$, 130.0, 118.2, 112.6, 61.5, 13.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{11} \mathrm{~N}_{4} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 243.0877$; found: 243.0866.

## Ethyl 4-(4-Nitrophenyl)-1H-1,2,3-triazole-5-carboxylate (3n) ${ }^{18}$

Eluent: EtOAc/PE (1:1); yield: 157 mg (31\%); white solid; mp 178$180^{\circ} \mathrm{C} ; R_{f}=0.45(\mathrm{PE} / \mathrm{EtOAC} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=8.29\left(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 8.10(\mathrm{~d}, \mathrm{~J}=$ $\left.9.0 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 4.37\left(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.34(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3$ $\mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=160.6,148.3,145.1,145.1,135.6$, 130.2, 123.1, 61.6, 13.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{~N}_{4} \mathrm{O}_{4}[\mathrm{M}+\mathrm{H}]^{+}$: 263.0775; found: 263.0768.

Ethyl 4-(Pyridin-3-yl)-1H-1,2,3-triazole-5-carboxylate (30) ${ }^{19}$
Eluent: EtOAc/PE (1:1); yield: 171 mg (35\%); white solid; mp 158$160^{\circ} \mathrm{C} ; R_{f}=0.48(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta=9.61\left(\mathrm{~s}, 1 \mathrm{H}_{\text {pyridyl }}\right), 9.33(\mathrm{~d}, \mathrm{~J}=4.8 \mathrm{~Hz}, 1$ $\left.\mathrm{H}_{\text {pyridyl }}\right), 8.86\left(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}_{\text {pyridyl }}\right), 8.22-8.18\left(\mathrm{~m}, 1 \mathrm{H}_{\text {pyridyl }}\right), 4.97(\mathrm{q}$, $\left.J=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.92\left(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=161.2,151.0,150.7,150.1,137.3$, 137.0, 125.6, 123.9, 61.6, 14.6.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{11} \mathrm{~N}_{4} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 219.0877$; found: 219.0870.

Ethyl 4-(Thiophen-2-yl)-1H-1,2,3-triazole-5-carboxylate (3p) ${ }^{5 \mathrm{~h}}$
Eluent: EtOAc/PE (1:2); yield: 118 mg (63\%); white solid; mp 144$146{ }^{\circ} \mathrm{C} ; R_{f}=0.50(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.97\left(\mathrm{~d}, J=3.8 \mathrm{~Hz}, 1 \mathrm{H}_{\text {thiophenyl }}\right), 7.56$ (d, $\left.J=4.9 \mathrm{~Hz}, 1 \mathrm{H}_{\text {thiophenyl }}\right), 7.14\left(\mathrm{dd}, J=4.9,3.8 \mathrm{~Hz}, 1 \mathrm{H}_{\text {thiophenyl }}\right), 4.42(\mathrm{q}, J=$ $\left.7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 1.40\left(\mathrm{t}, \mathrm{J}=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=160.8,138.6,136.3,130.5,129.5$, 127.9, 127.3, 61.4, 13.3.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{9} \mathrm{H}_{10} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{~S}[\mathrm{M}+\mathrm{H}]^{+}: 224.0488$; found: 224.0482.

## Ethyl 4-Propyl-1H-1,2,3-triazole-5-carboxylate (3q) ${ }^{20}$

Eluent: EtOAc/PE (1:1); yield: 104 mg (71\%); white solid; mp 93$95^{\circ} \mathrm{C} ; R_{f}=0.46(\mathrm{PE} / \mathrm{EtOAc} 1: 1)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta=4.41\left(\mathrm{q}, \mathrm{J}=7.1 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.04$ ( $\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), 1.79-1.67 (m, $2 \mathrm{H} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $1.35(\mathrm{t}$, $\left.J=7.1 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.94\left(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=161.9,146.3,135.2,61.4,26.2,22.4$, 14.4, 13.9.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{8} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}$: 184.1081; found: 184.1077.

## Phenyl(4-phenyl-1H-1,2,3-triazol-5-yl)methanone (5a) ${ }^{21}$

Eluent: EtOAc/PE (1:3); yield: 162 mg (43\%); white solid; mp 117$120^{\circ} \mathrm{C} ; R_{f}=0.62(\mathrm{PE} / \mathrm{EtOAC} 1: 1)$.
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=8.34-7.97\left(\mathrm{~m}, 2 \mathrm{H}_{\mathrm{arom}}\right), 7.97-6.94(\mathrm{~m}, 8$ $\mathrm{H}_{\text {arom }}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=188.4,171.6,146.2,133.8,130.8,130.4$, 130.0, 129.1, 128.8, 128.7, 128.6.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{15} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}[\mathrm{M}+\mathrm{H}]^{+}$: 250.0975; found: 250.0963.

## Phenyl[4-(p-tolyl)-1H-1,2,3-triazol-5-yl]methanone (5b) ${ }^{22}$

Eluent: EtOAc/PE (1:3); yield: 149 mg (38\%); white solid; mp 138$140^{\circ} \mathrm{C} ; R_{f}=0.62$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( 300 MHz, DMSO- $d_{6}$ ): $\delta=8.11\left(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right.$ ), $7.67-$ $7.59\left(\mathrm{~m}, 3 \mathrm{H}_{\text {arom }}\right), 7.48\left(\mathrm{t}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.22\left(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right)$, $2.39\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{ArCH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( 75 MHz, DMSO- $d_{6}$ ): $\delta=188.5,145.1,141.3,139.7,137.9$, 133.9, 130.8, 129.7, 129.2, 129.1, 125.9.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{16} \mathrm{H}_{14} \mathrm{~N}_{3} \mathrm{O}[\mathrm{M}+\mathrm{H}]^{+}: 264.1131$; found: 264.1130.

## Cyclopropyl(4-phenyl-1 $\mathbf{H - 1 , 2 , 3 - t r i a z o l - 5 - y l ) m e t h a n o n e ~ ( 5 c ) ~}$

Eluent: EtOAc/PE (1:2). Yield: 120 mg ( $56 \%$ ); white solid; mp 113$116^{\circ} \mathrm{C} ; R_{f}=0.59$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=7.82-7.54\left(\mathrm{~m}, 2 \mathrm{H}_{\text {arom }}\right)$, 7.54-7.19 ( $\mathrm{m}, 3$ $\mathrm{H}_{\text {arom }}$ ), 3.08-3.01 (m, 1 H, CH), 1.24-1.23 (m, $2 \mathrm{H}, \mathrm{CH}_{2}$ ), 1.05-1.01(m, 2 $\mathrm{H}, \mathrm{CH}_{2}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta=195.9,144.1,141.8,133.9,130.4,130.1$, 129.4, 128.6, 127.5, 29.9, 19.5, 12.9.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{12} \mathrm{~N}_{3} \mathrm{O}[\mathrm{M}+\mathrm{H}]^{+}$: 214.0975; found: 214.0968.

## 4-(4-Fluorophenyl)-1H-1,2,3-triazole-5-carbonitrile (5d) ${ }^{23}$

Eluent: EtOAc/PE (1:1); yield: 163 mg (56\%); white solid; mp 190$192^{\circ} \mathrm{C} ; R_{f}=0.37$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.97$ (dd, $J_{1}=6.8 \mathrm{~Hz}, J_{2}=11.6 \mathrm{~Hz}, 2$ $\mathrm{H}_{\text {arom }}$ ), 7.41-7.15 (m, $2 \mathrm{H}_{\text {arom }}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=165.7$ ( $\mathrm{d}, \mathrm{J}=247.6 \mathrm{~Hz}$ ), 147.1, 129.1 ( d , $J=8.6 \mathrm{~Hz}), 123.4,116.9,116.3(\mathrm{~d}, J=22.2 \mathrm{~Hz}), 112.7$.
HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{9} \mathrm{H}_{6} \mathrm{FN}_{4}[\mathrm{M}+\mathrm{H}]^{+}$: 189.0571; found: 189.0565.

Spectral data match with those previously reported in the literature. ${ }^{14}$

## 4-( $\boldsymbol{p}$-Tolyl)-1H-1,2,3-triazole-5-carbonitrile (5e) ${ }^{23}$

Eluent: EtOAc/PE (1:1); yield: 133 mg (67\%); white solid; mp 173$175^{\circ} \mathrm{C} ; R_{f}=0.38$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=7.81$ (d, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}$ ), $7.38(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}$ ), $2.43\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{ArCH}_{3}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=147.0,141.0,130.0,126.5,123.3$, 116.5, 112.9, 20.2.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{9} \mathrm{~N}_{4}[\mathrm{M}+\mathrm{H}]^{+}$: 185.0822; found: 185.0813.

## 4-(4-Methoxyphenyl)-1 $\mathbf{H}$-1,2,3-triazole-5-carbonitrile (5f) ${ }^{23}$

Eluent: EtOAc/PE (1:1); yield: 166 mg (61\%); white solid; mp 197$200^{\circ} \mathrm{C}$; $R_{f}=0.33$ (PE/EtOAc 1:1).
${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right): \delta=7.85\left(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}\right), 7.09(\mathrm{~d}, J=$ $8.9 \mathrm{~Hz}, 2 \mathrm{H}_{\text {arom }}$ ), 3.86 ( $\mathrm{s}, 3 \mathrm{H}, \mathrm{OCH}_{3}$ ).
${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}$ ): $\delta=161.8,128.2,118.3,116,1,114.6$, 113.0, 89.8, 54.8.

HRMS (ESI): $m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{9} \mathrm{~N}_{4} \mathrm{O}[\mathrm{M}+\mathrm{H}]^{+}$: 201.0771; found: 201.0775.

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## Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609720.

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