Supporting Information

Triazole-Imidazole (TA-IM) as Ultrafast Fluorescent Probes for Selective Ag⁺ Detection

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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on Agilent 400 MHz spectrometers/Varian 600 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl$_3$ (δ 7.26 ppm) or DMSO (2.50 ppm) for $^1$H and CDCl$_3$ (δ 77.00 ppm), DMSO (40.00 ppm) for $^{13}$C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on Agilent 6540 LC/QTOF spectrometer.

1.1 General procedure to synthesize 2a-2c

\[ RX + Cl\text{CO}Et \xrightarrow{n-BuLi, THF, -78^\circ C} R\text{CO}Et \]

n-BuLi (2.5M in Hexane solution) (9.53 mL, 23.835 mmol) was slowly added to the R$^1$-alkynes (22 mmol) in 22 ml dry THF at -78°C. After stirred at -78°C for 1 h, cathy chloride (27.24 mmol, 2.53 mL) was added to the system. The reaction was monitored by TLC. After reaction completion, saturated NH$_4$Cl (15 mL) was introduced in order to quench the reaction at room temperature. The aqueous layer was extracted with Ethyl
Acetate (EA). Organic phase was dried with anhydrous sodium sulfate and purified products 2a-2c by silica gel column chromatography (Hexane and EA).

1.2 General procedure to synthesize 3a-3d

\[
\begin{align*}
\text{O} & \quad \text{OEt} \\
\text{O} & \quad \text{Et} \\
\text{R}^1 & \quad \text{N} \\
\text{Et} & \quad \text{N} \\
\text{NaN}_3 & \quad \text{Na}_3 \\
\text{DMSO} & \quad \text{DMSO} \\
\text{O} & \quad \text{OEt} \\
\text{N} & \quad \text{N} \\
\text{Et} & \quad \text{Et} \\
\text{R}^1 & \quad \text{N} \\
\text{3} & \quad \text{3} \\
\end{align*}
\]

R\(^1\)-propionic Acid Ethyl Ester 2 (15.4 mmol) was dissolved in 100 mL DMSO. After stirring, NaN\(_3\) (2.8 g, 43.05 mmol) was slowly added to the mixture and refluxed for 6 h under 60 \(^\circ\)C. In order to quench the reaction, water was introduced to the system. After extraction by using ethyl acetate as extractant, organic phase was washed with saturated salt water to remove excess DMSO and dried with anhydrous sodium sulfate. Compound 3 was purified by silica gel column chromatography (Hexane and EA) to isolate the pure products 3a-3d.

1.3 General procedure to synthesize 3Xa-3Xe

\[
\begin{align*}
\text{O} & \quad \text{OEt} \\
\text{O} & \quad \text{Et} \\
\text{N} & \quad \text{NH} \\
\text{R}^1 & \quad \text{N} \\
\text{K}_2\text{CO}_3 & \quad \text{K}_2\text{CO}_3 \\
\text{Acetone,} \text{R}^2\text{Br} & \quad \text{Acetone,} \text{R}^2\text{Br} \\
\text{3} & \quad \text{3X} \\
\end{align*}
\]

Triazole 3a-3d (1 mmol), 6 mL of acetone, the anhydrous potassium carbonate (2 mmol) and benzyl bromide (1.5 mmol) were successively joint to 50 mL round bottom flask. Under the protection of nitrogen, the mixture was stirred at room temperature 12 h until raw material disappeared by TLC monitoring the reaction. The mixture was filtered to remove chloride anhydrous potassium carbonate and washed residue for three
times. We preserved the filtrate with purification by column chromatography. (Hexane and EA) to isolate the pure products $3\text{Xa}-3\text{Xe}$.

1.4 General procedure to synthesize $3\text{Y}$

$3$ (3 mmol) was dissolved in 30 mL dry THF, LiAlH$_4$ (4.5 mmol) was added under 0 °C and the mixture was stirred for 5-6 h at room temperature until full conversion was reached (monitored by TLC). The THF was removed by vacuum distillation. Then 6 M HCl was added to the mixture until pH=2. After the aqueous layer was extracted with EA, organic layer was dried by anhydrous NaSO$_4$. The solvent was removed by rotary evaporator. Product directly used in next step without further purification.

The alcohol (3 mmol, 1.0 equiv.) and TBS-Cl (15 mmol, 3.0 equiv, according to limiting reagent), I$_2$ (6 mmol, 2.0 equiv.) were dissolved in 3 mL dry DMF and the reaction was run at room temperature overnight. After reaction completion, the solvent was removed by rotary evaporator, the mixture was subjected to the silica gel column chromatography (Hexane and EA) to isolate the pure products $3\text{Ya-3Yb}$.

1.5 General procedure to synthesize $3\text{Z}$
3Y (4 mmol, 1.0 equiv), K$_2$CO$_3$ (8 mmol, 2.0 equiv), Cul (0.4 mmol, 0.1 equiv), L-proline (0.8 mmol, 0.2 equiv), and ArI (6 mmol, 1.5 equiv) was successively added to 10 mL vial under N$_2$. Then anhydrous DMSO (20 mL) was added by syringes. The tube was heated to 110 °C for 12 h. After cooling to the room temperature, the reaction mixture was added water (15 mL) and saturated NH$_4$Cl solution (5 mL). Then the aqueous layer was extracted with ethyl acetate (2×15 mL). The combined organic phases were washed with brine (10 mL), dried by anhydrous Na$_2$SO$_4$ and concentrated in vacuum. The mixture was subjected to the silica gel column chromatography (Hexane: EA=8:1) to isolate the pure products 3Za-3Zc.

1.6 General procedure to synthesize 4 (R$_2$=alkyl: Condition B)

3X (3 mmol) was dissolved in 30 mL dry THF, LiAlH$_4$ (4.5 mmol) was added and the mixture was stirred for 5-6 h at room temperature until full conversion was reached (monitored by TLC). The THF was removed by vacuum distillation. Then 6 M HCl was added to the mixture until pH=2. After the aqueous layer was extracted with EA, organic layer was dried by anhydrous Na$_2$SO$_4$. The solvent was removed by rotary evaporator. Product directly be used in next step without further purification. Triazole alcohol (3 mmol, 1.0 equiv) was dissolved in dry DCM (15 mL), then PCC (10 mmol) was added to the mixture, and the mixture was stirred for 4-5 h at room temperature until full conversion was reached (monitored by TLC). After reaction completion, the solvent was removed by rotary evaporator, the mixture was subjected to the silica gel column chromatography (Hexane:EA=6:1) to isolate the pure products 4a-4e.
1.7 General procedure to synthesize 4 (R²=aryl: Condition C)

3Z (3.0 mmol, 1.0 equiv) was dissolved in 30 mL dry THF, TBAF (4.5 mmol, 1.5 equiv) was added. The mixture was stirred for 0.5-1 h at room temperature until full conversion was reached (monitored by TLC). The THF was removed by vacuum distillation. Then added aqueous. After the aqueous layer was extracted with EA, organic layer was dried by anhydrous NaSO₄. The solvent was removed by rotary evaporator. Product directly be used in next step without further purification.

The alcohol (3 mmol, 1.0 equiv) was dissolved in dry DCM (15 mL, 0.2 M), then PCC (10 mmol, 3.3 equiv) was added to the mixture, and the mixture was stirred for 4-5 h at room temperature until full conversion was reached (monitored by TLC). After reaction completion, the solvent was removed by rotary evaporator, the mixture was subjected to the silica gel column chromatography (Hexane and EA) to isolate the pure products 4f-4h.

1.8 Procedure to synthesize 5
A 50 mL screwed vial was charged with the aldehyde 4 (2 mmol, 1.0 equiv), 1,2-diaminobenzene (2 mmol, 1.0 equiv) in 1 mL CH₃CH₂OH. The reaction was run at 60 °C for 4 h. Then another 15 mL CH₃CH₂OH was added to the vial and the reaction was run at 90 °C for 12 h. After the reaction was completed, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give desired triazole-imidazole product 5a-5k.

1.9 Procedure to synthesize 6a

4,5-diphenyl-2H-1,2,3-triazole was synthesized by the literature:


4,5-diphenyl-2H-1,2,3-triazole (2 mmol, 1.0 equiv) was dissolved in Acetone 12 mL, after that the anhydrous K₂CO₃ (4 mmol, 2.0 equiv) and R₂Br (3.0 mmol, 1.5 equiv) was added and the mixture was stirred for 12 h at 30 °C until full conversion was reached (monitored by TLC). After reaction completion, the solvent was removed by rotary evaporator, the mixture was subjected to the silica gel column chromatography (Hexane: EA=5:1) to isolate the pure products 6a.

1.10 Procedure to synthesize 6b
A 50 mL vial was charged with the triazole aldehyde substrate 4a (2 mmol, 1.0 equiv), 2-aminobenzenethiol (2 mmol, 218 mg, 1.0 equiv) in anhydrous CH₃OH (20 mL, 0.1 M) and I₂ (1 mmol, 252 mg, 1.0 equiv). And the reaction was run at 30 °C for 3-4 h. After the reaction was completed, the solvent was removed under reduced pressure and the mixture was subjected to the silica gel column chromatography (Hexane: EA=5:1) to give desired 1,2,3-triazol-thiazole product 6b.

1.11 Procedure to synthesize 6c

![Chemical structure of 6c](image)

Ethyl 5-(pyridin-2-yl)-2H-1,2,3-triazole-4-carboxylate was synthesized according the following literature, see:


Ethyl 5-(pyridin-2-yl)-2H-1,2,3-triazole-4-carboxylate (1 mmol, 1.0 equiv) was dissolved in Acetone 6 mL, after that the anhydrous K₂CO₃ (2 mmol, 2.0 equiv) and R²Br (1.5 mmol, 1.5 equiv) was added and the mixture was stirred for 12 h at 30 °C until full conversion was reached (monitored by TLC). After reaction completion, the solvent was removed by rotary evaporator, the mixture was subjected to the silica gel column chromatography (Hexane: EA=2:1) to isolate the pure products 6c.
II. Fluorescence property

**Fluorescence detection Procedures:** A series of stock solution of compound 1,2,3-triazole (TA) (0.2 mmol/L) was prepared by dissolving the corresponding amount of compound powder in ethanol in a 100 mL volumetric flask, which was stored in the dark. For fluorescence detection, 200 μL stock solutions (0.2 mmol/L) were diluted with 1800 μL ethanol in the sample tubes. The fluorescence spectra of mixed solutions were recorded in the 300-600 nm emission wavelength range with the corresponding excitation wavelength at room temperature (298 K) by F-2700 spectrofluorophotometer (HITACHI Co., Ltd., Japan). The entrance slit and exit slit were set at 2.5 nm and 5 nm for the fluorescent determinations, respectively.

**UV-vis absorption detection Procedures:** 200 μL stock solutions (0.2 mmol/L) were diluted with 800 μL ethanol in the sample tubes. UV-vis absorption spectra of mixed solutions were obtained in the 200-800 nm wavelength by UV-3100 UV-VISNIR recording spectrophotometer (Shimadzu, Japan).

**Quantum yield determination:** All the quantum yields of samples were determined by EI Fluorescence Spectroscopy-FLS 980, the sample was dissolved in EtOH, concentration was 0.2 mmol/L.

2.1 The fluorescence intensity of 1b with addition of various metal ions

![Figure S1. The fluorescence intensity of 1b with addition of various metal ions. Concentration: 1b, 2.0 μmol/L; metal ions, 2.0 μmol/L.](image-url)
2.2 The fluorescence emission of 5a-5d

![Fluorescence emission graph](image)

Figure S2. Fluorescence emission of compound 5a-5d. Concentration: 20 μmol/L in EtOH.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption (nm)</th>
<th>Excitation (λ(max))</th>
<th>Emission (λ(max))</th>
<th>Stokes Shift (nm)</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>250 (0.948), 291 (0.794)</td>
<td>290</td>
<td>343</td>
<td>52</td>
<td>77</td>
</tr>
<tr>
<td>5b</td>
<td>250 (0.798), 310 (0.716)</td>
<td>310</td>
<td>364</td>
<td>54</td>
<td>64</td>
</tr>
<tr>
<td>5c</td>
<td>309 (0.774)</td>
<td>309</td>
<td>246</td>
<td>37</td>
<td>45</td>
</tr>
<tr>
<td>5d</td>
<td>250 (0.930), 298 (0.744)</td>
<td>293</td>
<td>329</td>
<td>36</td>
<td>41</td>
</tr>
</tbody>
</table>

Table S1. Comparison of optical properties of 5a-5d.
2.3 The fluorescence emission of 5e-5h

![Fluorescence emission of compound 5e-5h. Concentration: 20 μmol/L in EtOH.]

**Figure S3.** Fluorescence emission of compound 5e-5h. Concentration: 20 μmol/L in EtOH.

**Table S2.** Comparison of optical properties of 5e-5h.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption (nm)</th>
<th>Excitation ($\lambda_{\text{max}}$)</th>
<th>Emission ($\lambda_{\text{max}}$)</th>
<th>Stokes Shift (nm)</th>
<th>$\Phi_{\text{PL}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5e</td>
<td>261 (0.903), 289 (0.710)</td>
<td>290</td>
<td>353</td>
<td>62</td>
<td>64</td>
</tr>
<tr>
<td>5f</td>
<td>252 (0.657), 294 (0.645)</td>
<td>293</td>
<td>349</td>
<td>56</td>
<td>86</td>
</tr>
<tr>
<td>5g</td>
<td>294 (1.046), 307 (0.828)</td>
<td>296</td>
<td>328</td>
<td>32</td>
<td>98</td>
</tr>
<tr>
<td>5h</td>
<td>250 (0.762), 292 (0.657)</td>
<td>292</td>
<td>341</td>
<td>49</td>
<td>72</td>
</tr>
</tbody>
</table>
2.4 The fluorescence emission of 5i-5k

![Graph showing fluorescence emission for compounds 5i-5k.](image)

**Figure S4.** Fluorescence emission of compound 5i-5k. Concentration: 20 μmol/L in EtOH.

**Table S3.** Comparison of optical properties of 5i-5k.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption (nm)</th>
<th>Excitation (λ&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>Emission (λ&lt;sub&gt;max&lt;/sub&gt;)</th>
<th>Stokes Shift (nm)</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5i</td>
<td>289 (0.734)</td>
<td>291</td>
<td>368</td>
<td>77</td>
<td>93</td>
</tr>
<tr>
<td>5j</td>
<td>250 (0.640), 307 (1.042)</td>
<td>309</td>
<td>378</td>
<td>69</td>
<td>66</td>
</tr>
<tr>
<td>5k</td>
<td>308 (0.903)</td>
<td>309</td>
<td>380</td>
<td>71</td>
<td>54</td>
</tr>
</tbody>
</table>
2.5 The fluorescence emission of 6a-6c

![Fluorescence emission of compound 6a-6c.](image)

**Figure S5.** Fluorescence emission of compound 6a-6c. Concentration: 20 μmol/L in EtOH.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption (nm)</th>
<th>Excitation (λmax)</th>
<th>Emission (λmax)</th>
<th>Stokes Shift (nm)</th>
<th>Φ&lt;sub&gt;PL&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>257 (0.732)</td>
<td>317</td>
<td>370</td>
<td>53</td>
<td>44</td>
</tr>
<tr>
<td>6b</td>
<td>221 (1.273), 254 (0.785), 302 (0.666)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6c</td>
<td>263 (0.0215), 270 (0.0211)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
III. TA-IM 5a as Ag⁺ sensor

**Procedures for the determination of Ag(I):** For Ag(I) determination, the solutions were added to a sample tube in the following sequence with a total volume of 2 mL: 20 μL of 5a stock solution (0.2 mmol/L), HEPES buffer solution (1.0 mmol/L, pH 7.0), 30 μL of different amounts of Ag(I). And then the mixture was mixed thoroughly and stood for 1 min before detection. The fluorescence spectra were recorded in the 300-500 nm emission wavelength range with an excitation wavelength of 290 nm. The entrance slit and exit slit were both set at 5 nm. All measurements were performed at room temperature (298 K).

3.1 The stability of 5a

![Figure S6](image)

**Figure S6.** The stability of 5a. Concentration: 5a, 2 μmol/L. EtOH: Hepes, v:v=1:99.
3.2 The anions selectivity and competition of 5a for Ag⁺ assay.

**Figure S7.** The fluorescence intensity of 5a upon the addition of different anions (black bars) and the addition of Ag⁺ (red bars); Concentration: 5a, 2.0 μmol/L; Ag⁺, 2.0 μmol/L; anions, 2.0 μmol/L. EtOH:Hepes, v:v=1:99

3.3 The interference of 5a for Ag⁺ assay.

**Figure S8.** The fluorescence intensity of 5a+Ag⁺ system with the interfering metal ions. Concentration: 5a, 2.0 μmol/L; Ag⁺, 2.0 μmol/L; interfering metal ions, 2.0 μmol/L. EtOH:Hepes, v:v=1:99
3.4 The ESI MS of 5a and 5a+Ag⁺

**Figure S9.** a) ESI Mass spectrum of complex 5a, the sample was dissolved in MeOH.

b) ESI Mass spectrum of complex 5a+Ag⁺, the sample was dissolved in MeOH, and the C₅₅: CAg⁺ = 1:1.
3.5 The Benesi-Hildebrand plot of $1/(F-F_0)$ versus $1/[\text{Ag}^+]$

![Benesi-Hildebrand plot graph]

**Figure S10.** Benesi-Hildebrand plot of $1/(F-F_0)$ versus $1/[\text{Ag}^+]$.

3.6 The lifetime of 5a and 5a+Ag$^+$

![Fluorescence lifetime graph]

**Figure S11.** Fluorescence lifetime measurement: 5a (black line) and 5a+Ag$^+$ (red line). Concentration: 5a, 2.0 μmol/L; Ag$^+$, 2.0 μmol/L. EtOH:Hepes, v:v=1:99
3.7 The photo-stability of 5a

Figure S12. The effect of irradiation time on the fluorescence intensity of 5a (2 μm).

3.8 The pH range

Figure S13. Effect of different pH on the fluorescence intensity of 5a (black line) and 5a+Ag⁺ (red line); Concentration: 5a, 2.0 μmol/L; Ag⁺, 2.0 μmol/L, the solutions were mixed acids (mediated by NaOH and a mixture of acid comprising of H₃PO₄, CH₃COOH, H₃BO₃).
3.9 The different buffer

![Figure S14](image-url).

Figure S14. Effect of different buffer solution.
3.10 The comparison with other probes

Table S5 Comparison of different fluorescent probes for the determination of Ag⁺

<table>
<thead>
<tr>
<th>Fluorescent probe</th>
<th>Linear range (μmol/L)</th>
<th>Detection limit (nmol/L)</th>
<th>Reaction time (min)</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BODIPY</td>
<td>0.5-4</td>
<td>-</td>
<td>-</td>
<td>THF</td>
<td>[1]</td>
</tr>
<tr>
<td>rhodamine derivative</td>
<td>0.1-5</td>
<td>130</td>
<td>120</td>
<td>EtOH/H₂O (1:4, v/v)</td>
<td>[2]</td>
</tr>
<tr>
<td>Am-GQDs</td>
<td>3.06×10²-9.27×10²</td>
<td>3.06×10⁴</td>
<td>-</td>
<td>H₂O</td>
<td>[3]</td>
</tr>
<tr>
<td>CdSe/ZnS Quantum Dots</td>
<td>1.0-40</td>
<td>1000</td>
<td>30</td>
<td>MOPS buffer</td>
<td>[4]</td>
</tr>
<tr>
<td>HACs/ssDNA</td>
<td>0.1-75</td>
<td>58</td>
<td>10</td>
<td>TE buffer</td>
<td>[5]</td>
</tr>
<tr>
<td>aka Au₃P₅ (0-102 μm)</td>
<td>0.02 ppm</td>
<td>0.02 ppm</td>
<td>-</td>
<td>chitosan polymer media</td>
<td>[6]</td>
</tr>
<tr>
<td>aka Au₃P₅ (185 nm)</td>
<td>9.6</td>
<td>0.33</td>
<td></td>
<td>EtOH/HEPES (1:99, v/v)</td>
<td>This work</td>
</tr>
</tbody>
</table>

References

IV. ORTEP Drawing of the Crystal Structure

X-ray Crystallography

The X-ray diffraction data were measured on Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu Kα INCOATEC ImuS micro-focus source (λ = 1.54178 Å). Indexing was performed using Apex3 [1]. Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space group was determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2017 [5-7] (full-matrix least-squares on F²) within OLEX2 interface program [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atom of –NH groups were found from difference Fourier map and were freely refined. All remaining hydrogen atoms were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters. Crystal data and refinement conditions are shown in Table 1-6. QL_TAIM_d and QL_TAIM_b: Presence of low intensity Q-peaks (0.4el/A³ and 0.8el/A³ respectively) on Fourier difference map close to six-member ring fused with imidazole ring tentatively suggests that the second minor conformational isomer could be present in the crystal. In both cases the disorder was not modeled due to low intensity of q-peaks suggesting less than 10% content of second conformer for which the fused ring system is rotated approximately 180 degrees along single bond connecting it to center ring of the molecule. This would cause the –CF₃ or –OCH₃ groups to be located at positions where the observed difference electron density peaks are. Both crystals diffracted weekly and were collected at long exposure times.

4.1 TA-IM-5a

Fig. 1. Asymmetric unit of QL_TAIM_A. Anisotropic displacement parameters were drawn at 50% probability. CCDC: 1835133

Table 1 Crystal data and structure refinement for QL_TAIM_a.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>QL_TAIM_a</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{17}N_{5}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>351.40</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100.0</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.7774(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>22.0334(4)</td>
</tr>
<tr>
<td>c/Å</td>
<td>14.1047(3)</td>
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<tr>
<td>α/°</td>
<td>90</td>
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<tr>
<td>β/°</td>
<td>104.4370(10)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å^3</td>
<td>3544.54(12)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>ρ_calc/g/cm^3</td>
<td>1.317</td>
</tr>
<tr>
<td>μ/mm^-1</td>
<td>0.644</td>
</tr>
<tr>
<td>F(000)</td>
<td>1472.0</td>
</tr>
<tr>
<td>Crystal size/mm^3</td>
<td>0.098 × 0.06 × 0.039</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (λ = 1.54178)</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>7.614 to 136.486</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14 ≤ h ≤ 14, -26 ≤ k ≤ 26, -16 ≤ l ≤ 16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>53076</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6450 [R_{int} = 0.0553, R_{sigma} = 0.0246]</td>
</tr>
</tbody>
</table>
Data/restraints/parameters 6450/0/495
Goodness-of-fit on $F^2$ 1.044
Final R indexes [$I > 2\sigma (I)$] $R_1 = 0.0352$, $wR_2 = 0.0786$
Final R indexes [all data] $R_1 = 0.0469$, $wR_2 = 0.0844$
Largest diff. peak/hole / e Å$^{-3}$ 0.16/-0.27

**Figure S15.** Intramolecular H-bond of 5a.

4.1 TA-IM-5b

**Fig.2.** Asymmetric unit of **QL_TAIM_B.** Anisotropic displacement parameters were drawn at 50% probability. CCDC:1835134
Table 2 Crystal data and structure refinement for TAIM_b.

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<td>Largest diff. peak/hole / e Å^{-3}</td>
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4.3 TA-IM-5d
Fig. 3. Asymmetric unit of QL_TAIM_d. Anisotropic displacement parameters were drawn at 50% probability. CCDC: 1835139

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<td>Index ranges</td>
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Table 4 Crystal data and structure refinement for QL_TAIEM_E.

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4.3 TA-IM-5k
Fig. 5. Asymmetric unit of **QL_TAIM_G**. Anisotropic displacement parameters were drawn at 50% probability. CCDC:1835141

### Table 5 Crystal data and structure refinement for **QL_TAIM_G**.

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<tr>
<td>Largest diff. peak/hole / e Å⁻³</td>
<td>0.33/-0.34</td>
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V. Compounds Characterization

ethyl 3-phenylpropionate

2b was prepared following the General Procedure 1.1 and purified by flash Chromatography (Hexane: EA = 20:1) as yellow oil. and 91% yield.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.62 – 7.53 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.31 (m, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.35 (td, $J = 7.1$, 2.0 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.96, 132.87, 130.52, 128.48, 119.55, 85.93, 80.64, 77.00, 61.99, 14.01.

HRMS (ESI): Calculated for C$_{11}$H$_{12}$O$_2$ (M+H)$^+$: 175.0754 Found: 175.0757.

ethyl 3-(4-methoxyphenyl)propionate

2b was prepared following the General Procedure 1.1 and purified by flash Chromatography (Hexane: EA = 20:1) as yellow oil. and 80% yield.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.38 (m, 2H), 6.99 – 6.74 (m, 2H), 4.28 (dd, $J = 7.8$, 6.3 Hz, 2H), 3.83 (d, $J = 1.6$ Hz, 3H), 1.35 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.39, 154.19, 134.79, 114.18, 111.28, 86.77, 80.06, 61.79, 55.27, 14.02.

HRMS (ESI): Calculated for C$_{12}$H$_{14}$O$_3$ (M+H)$^+$: 205.0859 Found: 205.0857.
ethyl 3-(4-(trifluoromethyl)phenyl) propiolate

2c was prepared following the General Procedure 1.1 and purified by flash Chromatography (Hexane: EA = 20:1) as yellow oil and 86% yield.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.85 – 7.43 (m, 4H), 4.32 (q, $J = 7.2$ Hz, 2H), 1.37 (t, $J = 7.2$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.55, 133.11, 131.95 (q, $J = 32.8$ Hz), 1255.52(q, $J = 3.8$ Hz), 124.84, 123.44(q, $J = 272.5$ Hz), 122.14, 83.74, 82.25, 62.37, 14.01.


ethyl 5-phenyl-2H-1,2,3-triazole-4-carboxylate

3a was prepared following the General Procedure 1.2 and purified by flash Chromatography (Hexane: EA = 1:1) as white solid and 99% yield.

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 7.76 (s, 2H), 7.57 – 7.39 (m, 3H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.32, 134.84, 129.78, 129.56, 128.68, 61.18, 14.42.

HRMS(ESI): Calculated for C$_{11}$H$_{12}$N$_3$O$_2^+$ (M+H)$^+$: 218.0924, Found: 218.0923.
ethyl 5-(4-methoxyphenyl)-2H-1,2,3-triazole-4-carboxylate

3b was prepared following the General Procedure 1.2 and purified by flash Chromatography (Hexane: EA = 1:1) as white solid. and 95% yield.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.80 (d, $J$ = 8.8 Hz, 2H), 6.97 (d, $J$ = 8.9 Hz, 2H), 4.40 (d, $J$ = 7.1 Hz, 2H), 3.85 (s, 3H), 1.35 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.24, 160.60, 144.71, 133.23, 130.57, 119.22, 113.65, 61.37, 55.18, 13.91.

HRMS(ESI): Calculated for C$_{12}$H$_{14}$N$_3$O$_3$+ (M+H)$^+$: 248.1030, Found: 248.1027.

ethyl 5-(4-(trifluoromethyl) phenyl)-2H-1,2,3-triazole-4-carboxylate

3c was prepared following the General Procedure 1.2 and purified by flash Chromatography (Hexane: EA = 1:1) as white solid. and 99% yield.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 16.03 (s, 1H), 8.06 (d, $J$ = 8.0 Hz, 2H), 7.87 (d, $J$ = 8.0 Hz, 2H), 4.34 (q, $J$ = 7.1 Hz, 2H), 1.30 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.03, 130.34, 130.05, 129.73(q, $J$ = 32.0 Hz), 128.66, 125.42(q, $J$ = 3.8 Hz), 124.5(q, $J$ = 272.1 Hz), 123.25, 61.45, 14.33.

HRMS(ESI): Calculated for C$_{12}$H$_{11}$F$_3$N$_3$O$_3$+ (M+H)$^+$: 286.0798, Found: 286.0770.
ethyl 2H-1,2,3-triazole-4-carboxylate

3d was prepared following the General Procedure 1.2 and purified by flash Chromatography (Hexane: EA = 1:1) as white solid and 95% yield.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 15.86 (s, 1H), 8.55 (d, 1H), 4.35 (q, $J = 7.0$ Hz, 2H), 1.33 (td, $J = 7.1$, 1.5 Hz, 3H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 161.07, 136.46, 128.17, 61.02, 14.64, 14.58.

HRMS(ESI): Calculated for C$_5$H$_7$N$_3$NaO$_2$ (M+Na)$^+$: 164.0436, Found: 164.0428.

ethyl 2-benzyl-5-phenyl-2H-1,2,3-triazole-4-carboxylate

3Xa was prepared following the General Procedure 1.3 and purified by flash Chromatography (Hexane: EA = 4:1) as white solid and 85% yield.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.39 (d, $J = 2.0$ Hz, 4H), 8.30 (s, 1H), 7.96 (dd, $J = 8.5$, 1.3 Hz, 1H), 7.87 (s, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 5.3$ Hz, 6H).

$^{13}$C NMR $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.20, 150.26, 136.02, 131.26, 129.24, 129.10, 128.80, 128.58, 128.19, 128.03, 61.44, 59.37, 14.18.

HRMS(ESI): Calculated for C$_{18}$H$_{18}$N$_3$O$_2$ $^+$ (M+H)$^+$: 308.1394, Found: 308.1401.
ethyl 2-benzyl-5-(4-methoxyphenyl)-2H-1,2,3-triazole-4-carboxylate

3Xb was prepared following the General Procedure 1.3 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as colorless oil. Yield = 85 %.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.88 – 7.68 (m, 2H), 7.44 – 7.29 (m, 5H), 7.01 – 6.90 (m, 2H), 5.65 (s, 2H), 4.40 (q, $J = 7.1$ Hz, 2H), 3.83 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.29, 160.23, 150.07, 135.51, 134.27, 130.57, 128.72, 128.47, 128.09, 121.79, 113.42, 61.31, 59.23, 55.17, 14.17.


ethyl 2-benzyl-5-(4-(trifluoromethyl) phenyl)-2H-1,2,3-triazole-4-carboxylate

3Xc was prepared following the General Procedure 1.3 and purified by flash Chromatography (Hexane: Ethyl Acetate = 5:1) as white solid. Yield = 80 %.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.97 (d, $J = 8.1$ Hz, 2H), 7.68 (d, $J = 8.2$ Hz, 2H), 7.48 – 7.30 (m, 5H), 5.68 (s, 2H), 4.42 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.01, 148.89, 136.32, 133.97, 133.02, 131.13, 130.82, 129.64, 128.89, 128.75, 128.28, 125.00, 61.69, 59.56, 14.19.
HRMS(ESI): Calculated for C_{19}H_{17}F_{3}N_{3}O_{2}^{+} (M+H)^{+}: 376.1267, Found: 376.1269.

![3Xd](image)

**ethyl 2-benzyl-2H-1,2,3-triazole-4-carboxylate**

3Xd was prepared following the General Procedure 1.3 and purified by flash Chromatography (Hexane: Ethyl Acetate = 5:1) as white solid. Yield = 81%.

^1H NMR (400 MHz, Chloroform-d) δ 8.06 (s, 1H), 7.46 – 7.24 (m, 5H), 5.64 (s, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H).

^13C NMR (101 MHz, CDCl₃) δ 160.52, 140.18, 137.23, 134.11, 128.76, 128.55, 128.13, 61.32, 59.30, 14.20.

HRMS(ESI): Calculated for C_{12}H_{13}N_{3}O_{2}^{+} (M+Na)^{+}: 254.0900, Found: 254.0892.

![3Xe](image)

**ethyl 2-butyl-5-phenyl-2H-1,2,3-triazole-4-carboxylate**

3Xe was prepared following the General Procedure 1.3 and purified by flash Chromatography (Hexane: Ethyl Acetate = 6:1) as colorless oil. Yield = 90%.

^1H NMR (400 MHz, Chloroform-d) δ 7.96 – 7.75 (m, 2H), 7.43 (d, J = 6.6 Hz, 3H), 4.51 (t, J = 7.2 Hz, 2H), 4.40 (d, J = 7.1 Hz, 2H), 2.02 (t, J = 7.5 Hz, 2H), 1.37 (q, J = 8.7, 7.1 Hz, 5H), 0.96 (t, J = 7.3 Hz, 3H).

^13C NMR (101 MHz, CDCl₃) δ 161.23, 149.65, 135.36, 129.56, 129.13, 128.96, 127.99, 61.29, 55.51, 31.55, 19.64, 14.14, 13.41.
4-(((tert-butyldimethylsilyl) oxy)methyl)-5-phenyl-2H-1,2,3-triazole

3Ya was prepared following the General Procedure 1.4 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 74%.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.90 – 7.81 (m, 2H), 7.51 – 7.37 (m, 3H), 4.95 (s, 2H), 0.91 (s, 9H), 0.12 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO) δ 145.09, 143.08, 131.27, 129.11, 128.56, 127.60, 56.77, 26.10, 18.31, -4.86.

HRMS(ESI): Calculated for C$_{15}$H$_{20}$N$_3$O$_2$+ (M+H)$^+$: 274.1550, Found: 274.1552.

4-(((tert-butyldimethylsilyl) oxy)methyl)-5-(4-methoxyphenyl)-2H-1,2,3-triazole

3Yb was prepared following the General Procedure 1.4 and purified by flash Chromatography (Hexane: Ethyl Acetate = 3:1) as white solid. Yield = 77%.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.90 – 7.81 (m, 2H), 7.51 – 7.37 (m, 3H), 4.95 (s, 2H), 0.91 (s, 9H), 0.12 (s, 6H).

$^{13}$C NMR (101 MHz, DMSO) δ 159.70, 145.01, 142.50, 128.94, 123.72, 129.11, 128.56, 127.60, 55.81, 55.63, 26.13, 18.32, -4.82.

HRMS(ESI): Calculated for C$_{16}$H$_{25}$N$_3$O$_2$Si$^+$ (M+H)$^+$: 320.1789, Found: 320.1741.
4-(((tert-butyldimethylsilyl) oxy)methyl)-2,5-diphenyl-2H-1,2,3-triazole

3Za was prepared following the General Procedure 1.5 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 85%.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 8.18 – 8.07 (m, 2H), 8.04 – 7.96 (m, 2H), 7.70 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.48 (ddd, $J = 7.9, 6.7, 4.3$ Hz, 4H), 7.44 – 7.38 (m, 1H), 7.38 – 7.29 (m, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 4.95 (d, $J = 0.8$ Hz, 2H), 0.91 (d, $J = 0.8$ Hz, 9H), 0.13 (d, $J = 0.9$ Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.52, 145.44, 139.76, 137.45, 129.20, 128.63, 128.53, 127.87, 127.21, 118.71, 56.76, 25.82, 18.28, -5.13.


4-(((tert-butyldimethylsilyl) oxy) methyl)-5-(4-methoxyphenyl)-2-phenyl-2H-1,2,3-triazole

3Zb was prepared following the General Procedure 1.5 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 88%.
\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 8.13\) (d, \(J = 8.1\) Hz, 2H), 8.02 – 7.96 (m, 2H), 7.51 (t, \(J = 7.8\) Hz, 2H), 7.36 (t, \(J = 7.4\) Hz, 1H), 7.09 – 6.97 (m, 2H), 4.95 (s, 2H), 3.90 (s, 3H), 0.94 (s, 9H), 0.16 (s, 6H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 158.83, 147.07, 144.94, 133.63, 130.55, 128.60, 128.38, 127.81, 120.19, 114.28, 56.75, 55.56, 25.84, 18.30, -5.12.

HRMS (ESI): Calculated for \(\text{C}_{22}\text{H}_{30}\text{N}_{3}\text{O}_{2}\text{Si}^+\) (M+H)^+: 396.2102, Found: 369.2077.

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\text{OTBS}
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\text{3Zc}
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2-(4-(((tert-butyldimethylsilyl) oxy)methyl)-5-phenyl-2H-1,2,3-triazol-2-yl)pyridine

\(3\text{Za}\) was prepared following the General Procedure 1.5 and purified by flash Chromatography (Hexane: Ethyl Acetate = 3:1) as white solid. Yield = 81%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta 8.71 – 8.56\) (m, 1H), 8.14 (d, \(J = 8.3\) Hz, 1H), 8.10 – 8.03 (m, 2H), 7.90 (td, \(J = 7.9, 1.6\) Hz, 1H), 7.46 (ddd, \(J = 13.5, 7.9, 6.2\) Hz, 3H), 7.32 (dd, \(J = 7.4, 4.8\) Hz, 1H), 4.99 (s, 2H), 0.90 (s, 9H), 0.13 (s, 6H).

\(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 150.79, 148.84, 148.72, 146.59, 138.70, 129.91, 128.79, 128.49, 128.06, 122.60, 113.61, 56.72, 25.73, 18.17, -5.26.


\[
\text{H}
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\[
\text{4a}
\]

2-benzyl-5-phenyl-2H-1,2,3-triazole-4-carbaldehyde
4a was prepared following the General Procedure 1.6 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 90%.

$^1$H-NMR $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.20 (s, 1H), 8.03 (dd, $J = 7.8, 1.8$ Hz, 2H), 7.55 – 7.33 (m, 8H), 5.67 (s, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ 184.17, 149.29, 142.95, 133.88, 129.69, 128.87, 128.74, 128.60, 128.47, 128.27, 59.51.

HRMS m/z (ESI) calcd. for C$_{16}$H$_{14}$N$_3$O$^+$ (M+H)$^+$ : 264.1131, found 264.1132.

![4b](image)

2-benzyl-5-(4-methoxyphenyl)-2H-1,2,3-triazole-4-carbaldehyde

4b was prepared following the General Procedure 1.6 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 80%.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.18 (d, $J = 0.7$ Hz, 1H), 8.16 – 7.89 (m, 2H), 7.55 – 7.30 (m, 5H), 6.97 (d, $J = 8.8$ Hz, 2H), 5.65 (s, 2H), 3.85 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.37, 160.73, 149.18, 142.65, 133.97, 130.11, 128.90, 128.75, 128.27, 121.29, 113.88, 59.49, 55.28.

HRMS m/z (ESI) calcd. for C$_{17}$H$_{16}$N$_3$O$_2$ (M+H)$^+$ : 294.1237, found 294.1234.

![4c](image)

2-benzyl-5-(4-(trifluoromethyl) phenyl)-2H-1,2,3-triazole-4-carbaldehyde

4c was prepared following the General Procedure 1.6 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 90%.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 10.20 (s, 1H), 8.38 – 7.97 (m, 2H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.57 – 7.35 (m, 5H), 5.68 (s, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.30, 147.54, 143.31, 133.64, 132.27, 131.54 (q, $J = 32.6$ Hz), 131.22, 129.00, 128.95, 128.37, 125.46, 125.42 (q, $J = 3.8$ Hz), 125.38, 125.35, 122.57, 59.74.
HRMS m/z (ESI) calcd. for C_{17}H_{13}F_{3}N_{3}O^{+} (M+H)^{+} : 332.1005, found 332.1000.

\[ 
\text{H} \quad \text{O} \\
\text{H} \quad \text{N} \quad \text{N} \quad \text{Bn} \\
\]

\textbf{4d}

\textbf{2-benzyl-2H-1,2,3-triazole-4-carbaldehyde}

\textit{4d} was prepared following the General Procedure \textbf{1.6} and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 83%.

\textbf{1H NMR} (400 MHz, Chloroform-\textit{d}) \( \delta \) 10.10 (s, 1H), 8.09 (s, 1H), 7.37 (s, 5H), 5.66 (s, 2H).

\textbf{13C NMR} (101 MHz, CDCl\textit{3}) \( \delta \) 184.14, 147.35, 134.94, 133.88, 128.97, 128.85, 128.29, 59.50.

HRMS m/z (ESI) calcd. for C_{10}H_{10}N_{3}O^{+} (M+H)^{+} : 188.0818, found 188.0810.

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\text{H} \quad \text{O} \\
\text{H} \quad \text{N} \quad \text{N} \quad \text{Bn} \\
\]

\textbf{4e}

\textbf{2-butyl-5-phenyl-2H-1,2,3-triazole-4-carbaldehyde}

\textit{4e} was prepared following the General Procedure \textbf{1.6} and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 90%.

\textbf{1H NMR} (400 MHz, Chloroform-\textit{d}) \( \delta \) 9.99 (s, 1H), 8.16 (dd, J = 7.1, 1.6 Hz, 1H), 7.66 (d, J = 6.0 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.32 – 7.30 (m, 1H), 4.53 (t, J = 7.2 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.45 (q, J = 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H).

\textbf{13C NMR} (101 MHz, CDCl\textit{3}) \( \delta \) 184.24, 148.95, 142.43, 129.63, 128.92, 128.55, 128.51, 55.60, 31.39, 19.63, 13.39.

HRMS m/z (ESI) calcd. for C_{13}H_{16}N_{3}O^{+} (M+H)^{+} : 230.1288, found 230.1284.
2,5-diphenyl-2H-1,2,3-triazole-4-carbaldehyde

4f was prepared following the General Procedure 1.7 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 88%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 10.34 (s, 1H), 8.26 – 8.19 (m, 2H), 8.19 – 8.12 (m, 2H), 7.60 – 7.42 (m, 6H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.44, 149.77, 143.61, 139.11, 130.06, 129.52, 128.93, 128.85, 128.67, 128.64, 119.49.

HRMS m/z (ESI) calcd. for C\(_{15}\)H\(_{12}\)N\(_3\)O\(_2\)\(^+\) (M+H\(^+\)) : 250.0975, found 250.0968.

5-(4-methoxyphenyl)-2-phenyl-2H-1,2,3-triazole-4-carbaldehyde

4g was prepared following the General Procedure 1.7 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 83%.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 10.32 (s, 1H), 8.23 – 8.18 (m, 2H), 8.18 – 8.14 (m, 2H), 7.55 (dd, \(J = 8.6, 7.1\) Hz, 2H), 7.48 – 7.42 (m, 1H), 7.07 – 6.99 (m, 2H), 3.89 (s, 3H).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 184.55, 161.01, 149.53, 143.31, 139.10, 130.06, 129.45, 128.76, 121.15, 119.39, 113.98, 55.34.

HRMS m/z (ESI) calcd. for C\(_{16}\)H\(_{14}\)N\(_3\)O\(_2\)\(^+\) (M+H\(^+\)) : 280.1081, found 280.1082.
5-phenyl-2-(pyridin-2-yl)-2H-1,2,3-triazole-4-carbaldehyde

4h was prepared following the General Procedure 1.7 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 92%.

$^1$H NMR (400 MHz, Chloroform-d): δ 10.27 (s, 1H), 8.67-8.66 (m, 1H), 8.67-8.66 (m, 1H), 8.18-8.14 (m, 2H), 8.08-8.06 (m, 2H), 7.62 (ddd, J = 6.7, 4.9, 1.7 Hz, 1H), 7.57-7.53 (m, 3H)

$^{13}$C NMR (151 MHz, DMSO) δ 185.35, 150.14, 149.62, 149.53, 144.37, 140.41, 130.53, 129.48, 129.08, 129.05, 128.66, 125.39, 115.34.

HRMS m/z (ESI) calcd. for C_{14}H_{11}N_{4}O^+ (M+H)^+: 251.0927, found 251.0925.

![5a](attachment:image)

2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5a was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =72%.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 13.12 (s, 1H), 8.04 (d, J = 6.9 Hz, 2H), 7.69 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.48 – 7.33 (m, 8H), 7.26 (dd, J = 12.3, 7.6 Hz, 2H), 5.83 (s, 2H).

$^{13}$C NMR (101 MHz, DMSO) δ 150.38, 149.37, 148.09, 143.87, 140.31, 138.79, 134.94, 129.87, 129.70, 129.56, 129.44, 128.79, 124.75, 123.89, 122.41, 119.88, 114.90, 112.28.

HRMS m/z (ESI) calcd. for C_{22}H_{18}N_{5}^+(M+H)^+: 352.1557, found:352.1549.
2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl)-6-methoxy-1H-benzo[d]imidazole

5b was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =67%.

\[ \text{NMR (600 MHz, DMSO-}d_6\text{)} \delta 12.79 \text{ (d, } J = 17.3 \text{ Hz, 1H), 8.19 (d, } J = 7.6 \text{ Hz, 2H), 7.63 – 6.98 (m, 10H), 6.87 (dd, } J = 33.1, 8.6 \text{ Hz, 1H), 5.82 (s, 2H), 3.80 (s, 3H).} \]

\[ \text{C NMR (151 MHz, DMSO)} \delta 156.89, 155.93, 146.03, 145.84, 144.59, 144.42, 143.37, 138.30, 136.71, 135.77, 135.51, 130.22, 129.20, 129.15, 128.88, 128.65, 128.34, 120.16, 113.61, 112.30, 111.91, 101.81, 94.85, 58.78, 55.88. \]

HRMS m/z (ESI) calcd. For C_{23}H_{20}N_{5}O^{+} (M+H)^{+}: 382.1662 found: 382.1663

2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole-6-carbonitrile

5c was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =76%.

\[ \text{NMR (600 MHz, DMSO-}d_6\text{)} \delta 13.27 \text{ (s, 1H), 8.20 – 8.00 (m, 3H), 7.75 (d, } J = 8.1 \text{ Hz, 1H), 7.65 – 7.53 (m, 1H), 7.52 – 7.30 (m, 8H), 5.83 (s, 2H).} \]

\[ \text{C NMR (151 MHz, DMSO)} \delta 146.75, 143.28, 138.07, 135.69, 135.56, 129.84, 129.41, 129.26, 129.22, 129.03, 128.73, 128.70, 128.38, 126.84, 124.60, 120.23, 116.78, 113.44, 104.57, 58.96. \]

HRMS m/z (ESI) calcd. For C_{23}H_{17}N_{6}O^{+} (M+H)^{+}= 377.1509 found: 377.1506.
2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl)-6-(trifluoromethyl)-1H benzimidazole

5d was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 81%.

$^1$H NMR (600 MHz, DMSO-d$_6$) δ 13.39 (s, 1H), 8.16 – 8.10 (m, 2H), 7.95 (s, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.55 (dd, J = 8.4, 1.7 Hz, 1H), 7.48 (dd, J = 8.2, 6.3 Hz, 2H), 7.46 – 7.39 (m, 5H), 7.38 – 7.34 (m, 1H), 5.85 (s, 2H).

$^{13}$C NMR (151 MHz, DMSO) δ 146.75, 146.42, 135.74, 135.22, 129.72, 128.92, 128.81, 128.65, 128.33, 128.27, 128.21, 128.04, 127.79, 125.99 (q, J = 271.7 Hz), 124.19, 123.63, 123.42 (q, J = 32.0 Hz), 123.21, 123.00, 119.12, 58.72.

HRMS m/z (ESI) calcd. For C$_{23}$H$_{17}$F$_3$N$_5$ (M+H)$^+$ = 420.1431 found: 420.1431.

2-(2-benzyl-5-(4-methoxyphenyl)-2H-1,2,3-triazol-4-yl)-1H-benzimidazole

5e was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 83%.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 12.92 (s, 1H), 8.16 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.44 – 7.35 (m, 4H), 7.28 – 7.15 (m, 2H), 7.03 (dd, J = 8.7, 1.4 Hz, 2H), 5.80 (s, 2H), 3.81 (d, J = 1.3 Hz, 3H).
**13C NMR** (101 MHz, DMSO) δ 160.20, 146.10, 144.60, 143.81, 136.07, 135.90, 134.82, 130.39, 129.28, 128.74, 128.40, 123.50, 122.54, 122.19, 119.63, 114.17, 112.06, 58.78, 55.67.

**HRMS** m/z (ESI) calcd. For C23H20N5O+(M+H)= 382.1662 found: 382.1665.

2-(2-benzyl-5-((trifluoromethyl)phenyl)-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5f was prepared following the General Procedure 1.8 and purified by flash chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield = 71%.

**1H NMR** (400 MHz, DMSO-d6) δ 13.05 (s, 1H), 8.44 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.48 – 7.33 (m, 5H), 7.25 (dt, J = 14.1, 7.4 Hz, 2H), 5.86 (s, 2H).

**13C NMR** (101 MHz, DMSO) δ 144.77, 144.02, 143.75, 137.16, 135.61, 134.87, 134.23, 129.77, 129.30, 128.83, 128.48, 126.05, 125.65, 123.71, 123.35, 122.33, 119.75, 112.18, 59.04.

**HRMS** m/z (ESI) calcd. For C23H16N5F3+(M+H)= 420.1431 found: 420.1429.

2-(2-benzyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5g
5g was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =79%.

\[ ^1H \text{ NMR (400 MHz, DMSO-}d_6) \delta 13.06 \text{ (s, 1H), 8.40 \text{ (s, 1H), 7.66 \text{ (d, } J = 7.6 \text{ Hz, 1H), 7.50 \text{ (d, } J = 7.6 \text{ Hz, 1H), 7.44} - 7.30 \text{ (m, 5H), 7.28} - 7.13 \text{ (m, 2H), 5.79 \text{ (s, } 2H)}).} \]

\[ ^{13}C \text{ NMR (101 MHz, DMSO) } \delta 144.06, 140.77, 135.98, 134.21, 129.21, 128.67, 128.33, 122.98, 118.98, 112.11, 58.69. \]

HRMS m/z (ESI) calcd. For C_{16}H_{14}N_5^+ (M+H)^+= 276.1244 found: 276.1244.

![5h](image)

2-(2-butyl-5-phenyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5h was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =85%.

\[ ^1H \text{ NMR (400 MHz, DMSO-}d_6) \delta 12.93 \text{ (s, 1H), 8.24} - 8.11 \text{ (m, 2H), 7.67 \text{ (d, } J = 7.9 \text{ Hz, 1H), 7.53 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.46 \text{ (dt, } J = 13.2, 6.7 \text{ Hz, 3H), 7.23 \text{ (dd, } J = 13.9, \text{ 7.7 Hz, 2H), 4.58 \text{ (t, } J = 7.0 \text{ Hz, 2H), 1.98 \text{ (q, } J = 7.3 \text{ Hz, 2H), 1.38 \text{ (q, } J = 7.4 \text{ Hz, 2H), 0.94 \text{ (t, } J = 7.4 \text{ Hz, 3H).} \}

\[ ^{13}C \text{ NMR (101 MHz, DMSO) } \delta 145.64, 144.59, 143.82, 135.93, 134.82, 130.38, 129.17, 128.91, 128.72, 123.46, 122.18, 119.64, 112.04, 55.10, 31.59, 19.72, 13.87. \]

HRMS m/z (ESI) calcd. For C_{19}H_{20}N_5^+ (M+H)^+= 318.1713 found: 318.1714.

![5i](image)

2-(2,5-diphenyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole
5i was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =89%.

$^1$H NMR (600 MHz, DMSO-$d_6$) δ 13.13 (s, 1H), 8.35 – 8.28 (m, 2H), 8.26 – 8.19 (m, 2H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.60 (d, $J$ = 7.9 Hz, 1H), 7.56 – 7.48 (m, 4H), 7.33 – 7.28 (m, 1H), 7.27 – 7.22 (m, 1H).

$^{13}$C NMR (151 MHz, DMSO) δ 147.46, 143.99, 143.86, 139.17, 137.95, 134.82, 130.33, 129.75, 129.26, 128.97, 128.82, 123.84, 122.37, 119.84, 119.24, 112.14.

HRMS m/z (ESI) calcd. For C$_{21}$H$_{16}$N$_5$ (M+H)$^+$= 338.1400 found: 338.1401.

![5j](image)

2-(5-(4-methoxyphenyl)-2-phenyl-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5j was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 4:1) as white solid. Yield =77%.

$^1$H NMR (600 MHz, DMSO-$d_6$) δ 13.10 (s, 1H), 8.35 – 8.28 (m, 2H), 8.26 – 8.13 (m, 2H), 7.73 (s, 1H), 7.69 – 7.63 (m, 2H), 7.60 (s, 1H), 7.54 – 7.48 (m, 1H), 7.27 (d, $J$ = 22.9 Hz, 2H), 7.13 – 7.06 (m, 2H), 3.84 (s, 3H).

$^{13}$C NMR (151 MHz, DMSO) δ 160.56, 147.32, 144.22, 143.88, 139.19, 137.48, 134.79, 130.71, 130.28, 128.80, 123.66, 122.41, 122.05, 119.75, 119.13, 114.25, 112.05, 55.71.

HRMS m/z (ESI) calcd. For C$_{22}$H$_{17}$N$_5$O (M+H)$^+$= 368.1506 found: 368.1504.
2-(5-phenyl-2-(pyridin-2-yl)-2H-1,2,3-triazol-4-yl)-1H-benzo[d]imidazole

5i was prepared following the General Procedure 1.8 and purified by flash Chromatography (Hexane: Ethyl Acetate = 3:1) as white solid. Yield = 82%.

$^{1}$H NMR (600 MHz, DMSO-$d_6$) $\delta$ 13.23 (s, 1H), 8.67 (dd, $J$ = 4.7, 1.7 Hz, 1H), 8.37 – 8.27 (m, 2H), 8.23 (d, $J$ = 8.1 Hz, 1H), 8.17 (td, $J$ = 7.8, 1.9 Hz, 1H), 7.72 (d, $J$ = 8.0 Hz, 1H), 7.59 (dd, $J$ = 7.4, 4.8 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.27 (dt, $J$ = 36.1, 7.5 Hz, 2H).

$^{13}$C NMR (151 MHz, DMSO) $\delta$ 150.36, 149.32, 148.05, 143.81, 140.24, 138.75, 134.88, 129.80, 129.65, 129.37, 128.73, 124.70, 123.81, 122.33, 119.81, 114.88, 112.20.

HRMS m/z (ESI) calcd. For C$_{20}$H$_{15}$N$_6$+ (M+H)$^+$ = 339.1353 found: 339.1352.

2-benzyl-4,5-diphenyl-2H-1,2,3-triazole

6a was prepared following the General Procedure 1.9 and purified by flash Chromatography (Hexane: Ethyl Acetate = 5:1) as white solid. Yield = 87%.

$^{1}$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.55 (dd, $J$ = 6.7, 3.0 Hz, 4H), 7.46 – 7.40 (m, 2H), 7.39 – 7.28 (m, 9H), 5.64 (s, 2H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.76, 135.27, 130.99, 128.71, 128.53, 128.48, 128.37, 128.25, 128.09, 58.70.

HRMS m/z (ESI) calcd. For C$_{21}$H$_{18}$N$_3$+ (M+H)$^+$ = 312.1495 found: 312.1493.

![6b](image)

2-(2-benzyl-5-phenyl-2H-1,2,3-triazol-4-yl) benzo[d]triazole
6b was prepared following the General Procedure 1.10 and purified by flash Chromatography (Hexane: Ethyl Acetate = 5:1) as yellow solid. Yield =72%.

$^1$H NMR (400 MHz, Chloroform-d) δ 8.12 – 7.98 (m, 3H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.52 – 7.42 (m, 6H), 7.37 (td, $J = 10.7, 9.2, 7.0$ Hz, 4H), 5.69 (s, 2H).

$^{13}$C NMR (101 MHz, DMSO) δ 158.91, 153.52, 146.02, 138.85, 135.54, 134.90, 134.90, 129.74, 129.37, 129.33, 128.88, 128.81, 128.66, 127.11, 126.49, 123.64, 122.70, 58.95.

HRMS m/z (ESI) calcd. For C$_{22}$H$_{17}$N$_4$S+ (M+H)$^+$ = 369.1168 found: 369.1165.

![6c](image)

ethyl 2-benzyl-5-(pyridin-2-yl)-2H-1,2,3-triazole-4-carboxylate
6a was prepared following the General Procedure 1.9 and purified by flash Chromatography (Hexane: Ethyl Acetate = 2:1) as pale yellow solid. Yield =80%.
$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.77 (d, $J$ = 4.9 Hz, 1H), 7.73 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.53 (d, $J$ = 7.9 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.22 – 7.10 (m, 3H), 7.00 – 6.90 (m, 2H), 5.82 (s, 2H), 4.36 (q, $J$ = 7.1 Hz, 2H), 1.33 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.94, 149.30, 145.84, 138.81, 136.98, 136.30, 134.57, 128.48, 128.11, 127.61, 127.04, 124.25, 77.32, 77.24, 76.93, 76.68, 76.61, 61.17, 52.72, 14.08.

HRMS m/z (ESI) calcd. For C$_{17}$H$_{17}$N$_4$O$_2$ ($M + H$)$^+$ = 309.1346 found: 309.1327.
III. NMR Spectra Data
$^1$H NMR of compound 2a

![NMR Spectrum of 2a](image)
$^{13}$C NMR of compound 2a

2a

![C NMR spectrum of 2a](image)
$^1$H NMR of compound 2b
$^{13}$C NMR of compound 2b
$^1$H NMR of compound 2c
$^{13}$C NMR of compound 2c
$^1$H NMR of compound 3a
$^{13}$C NMR of compound 3a
$^1$H NMR of compound 3b
$^{13}$C NMR of compound 3b
$^1$H NMR of compound 3c
$^{13}$C NMR of compound 3c

![NMR spectrum of compound 3c](image-url)
$^1$H NMR of compound 3d

![NMR Spectrum of Compound 3d](image-url)
$^{13}$C NMR of compound 3d
$^1$H NMR of compound 3Xa
$^{13}$C NMR of compound 3Xa

![Carbon NMR spectrum of compound 3Xa]
$^1$H NMR of compound 3Xb

3Xb
$^{13}$C NMR of compound 3Xb
$^1$H NMR of compound 3Xc
$^{13}$C NMR of compound 3Xc

![C NMR spectrum of compound 3Xc](image)

**3Xc**

- 161.01
- 148.89
- 131.13
- 130.82
- 129.89
- 128.28
- 125.00
- 69.66
- 61.69
- 77.00
- 14.19
$^1$H NMR of compound 3Xd
$^{13}$C NMR of compound 3Xd

![13C NMR spectrum of compound 3Xd with chemical shifts at various positions]

Chemical shifts:
- 160.52
- 140.18
- 137.23
- 134.11
- 131.16
- 128.55
- 128.13
- 77.00
- 61.32
- 60.30
- 14.20
$^1$H NMR of compound 3Xe
$^{13}$C NMR of compound 3Xe
$^1$H NMR of compound 3Ya
$^{13}$C NMR of compound 3Ya
$^1$H NMR of compound 3Yb

![NMR spectrum image]

3Yb
$^{13}$C NMR of compound 3Yb
$^1$H NMR of compound 3Za
$^{13}$C NMR of compound 3Za

![NMR spectrum of 3Za with chemical shifts and peaks labeled.]
$^1$H NMR of compound 3Zb
$^{13}$C NMR of compound 3Zb
$^1$H NMR of compound 3Zc
$^{13}$C NMR of compound 3Zc
$^1$H NMR of compound 4a
$^{13}$C NMR of compound 4a
$^1$H NMR of compound 4b
$^{13}$C NMR of compound 4b

![NMR spectrum of compound 4b](image)
$^1$H NMR of compound 4c
$^{13}$C NMR of compound 4c
$^1$H NMR of compound 4d
$^{13}$C NMR of compound 4d
$^1$H NMR of compound 4e
$^{13}$C NMR of compound 4e

![Chemical structure of compound 4e]

- 184.24
- 148.95
- 142.43
- 129.03
- 128.97
- 128.55
- 128.51
- 77.00
- 55.60
- 31.39
- 19.63
- 13.39

![NMR spectrum of compound 4e]
$^1$H NMR of compound 4f

![NMR Spectrum](image-url)
$^{13}$C NMR of compound 4f
$^1$H NMR of compound 4g
$^{13}$C NMR of compound 4g

![NMR spectrum of compound 4g with chemical shifts and peak assignments]
$^1$H NMR of compound 4h
$^{13}$C NMR of compound 4h
$^1$H NMR of compound 5a
$^{13}$C NMR of compound 5a

![Chemical Structure](image)

5a
$^1$H NMR of compound 5b
$^{13}$C NMR of compound $5b$
$^1$H NMR of compound 5c
$^{13}$C NMR of compound 5c

[Chemical structure diagram]

146.75, 143.28, 138.07, 135.56, 134.18, 129.91, 129.88, 129.22, 129.03, 128.72, 128.64, 128.38, 124.00, 116.78, 114.57

-68.96
$^1$H NMR of compound 5d
$^{13}$C NMR of compound 5d
$^1$H NMR of compound 5e
13C NMR of compound 5e
$^1$H NMR of compound 5f

![NMR spectrum of compound 5f]
$^{13}$C NMR of compound 5f

![NMR Spectrum](image-url)
$^1$H NMR of compound 5g
$^{13}$C NMR of compound 5g
$^1$H NMR of compound 5h
$^{13}$C NMR of compound 5h
$^1$H NMR of compound 5i
$^{13}$C NMR of compound 5i
$^1$H NMR of compound 5j
$^{13}$C NMR of compound 5j
$^1$H NMR of compound 5k

[Image of the NMR spectrum showing various chemical shifts]
$^{13}$C NMR of compound 5k

![NMR spectrum of compound 5k]
$^1$H NMR of compound 6a
$^{13}$C NMR of compound 6a
$^1$H NMR of compound 6b

![NMR spectrum of 6b](image)
$^{13}$C NMR of compound 6b
$^1$H NMR of compound 6c
$^{13}$C NMR of compound 6c

![NMR spectrum of compound 6c]