Design and Green Synthesis of Novel Benzotriazoloquinolinyl Spirooxindolopyrrolizidines: Antimycobacterial and Antiproliferative studies

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Supplementary Information

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of compounds 1a-g and reusability studies of the ionic liquid</td>
<td>2-3</td>
</tr>
<tr>
<td>2</td>
<td>General information, crystallographic data information and biological assays</td>
<td>3-5</td>
</tr>
<tr>
<td>3</td>
<td>Spectral data and Copies of the characterization spectra (1H-NMR, 13C-NMR, IR &amp; mass spectra) of the synthesized compounds 4a-p.</td>
<td>5-43</td>
</tr>
<tr>
<td>4</td>
<td>Characterization spectral data and spectral copies (1H-NMR, 13C-NMR) of the synthesized compounds 1a-g.</td>
<td>44-53</td>
</tr>
</tbody>
</table>
1. Procedure for the synthesis of the dipolarophiles 1a-g

The equal mmol of compound 2-(1H-benzo[d][1,2,3]triazol-1-yl)quinoline-3-carbaldehyde (1 mmol) and various acetophenones (1 mmol) were mixed in 5 mL of ethanol and added 1 mL of 20% ethanolic sodium hydroxide. Then the reaction was stirred at room temperature for an appropriate time. The progress of the reaction was monitored by TLC. The solid product was formed in the reaction and it was collected by filtration, washed with cold ethanol and dried under vacuum to afford the dipolarophiles 1a-g.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

Scheme S1: Synthesis of the chalcone 1a-g.

1.2. Procedure for the synthesis of the 2-(1H-benzo[d][1,2,3]triazol-1-yl)quinoline-3-carbaldehyde

The mixture of compounds 2-chloroquinoline-3-carbaldehyde (1 mmol) and 1H-benzo[d][1,2,3]triazole (1.5 mmol) and K₂CO₃ (2 mmol) were mixed in 5 mL of DMF and refluxed for 2 h. The progress of the reaction was monitored by TLC and after completion of starting materials the mixture was cooled to room temperature and poured on ice cold water results the solid product. It was collected by filtration and dried under vacuum to afford the 2-(1H-benzo[d][1,2,3]triazol-1-yl)quinoline-3-carbaldehyde.

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

Scheme S2: Synthesis of the 2-(1H-benzo[d][1,2,3]triazol-1-yl)quinoline-3-carbaldehyde.
1.3. Reusability studies of ionic liquid

Although the \([\text{Bmim}]\text{BF}_4\) working efficiently as a medium and also as a catalyst, further, we have investigated the scope and efficiency with respect to the reusability and catalytic activity. After ensuring the completion of the reaction, the reaction mixture was added to 20 mL of ice-cold water and results in the desired solid product which was isolated by the filtration. The aqueous filtrate was evaporated under the reduced pressure followed by washing with diethyl ether (2 x 20 mL) then reused the \([\text{Bmim}]\text{BF}_4\) for four subsequent runs without significant change of yields and catalytic activity.

![Figure A: Reusability study of the \([\text{Bmim}]\text{BF}_4\) for the synthesis of spirooxindolopyrrolizidine derivatives.]

2.1. General information

All the chemicals and solvents were purchased from Aldrich/Spectrochem. All melting points were checked by using Stuart SMP30 melting point apparatus (Bibby Scientific Ltd. United Kingdom) and were uncorrected. Ultrasonication irradiation was performed on PCi-Analytics-6.5L200H1DTC ultrasonic cleaner, the frequency of ultrasonic cleaner is 25 kHz, input voltage range of 170–270 VAC at 50 Hz, and output power is 250 W
(Mumbai, India). The reaction progress was checked with TLC plates (E. Merck, Mumbai, India). IR spectra were recorded on KBr disc by using Perkin-Elmer 100S spectrophotometer (Perkin-Elmer Ltd. United Kingdom) from 400-4000 cm\(^{-1}\). \(^1\)H and \(^{13}\)C NMR spectra were recorded on Avance-III Bruker-400 MHz spectrometer (Bruker Corporation Ltd., Germany) using DMSO-\(d_6\) as solvent and TMS as an internal standard and chemical shifts values were expressed in ppm. The CHN analysis was recorded on Carlo Erba EA 1108 automatic analyzer (Triad, NJ, USA) and the values are ±0.4% of theoretical values. Mass spectra were determined on a Jeol JMSD-300 spectrometer (Jeol Ltd., Tokyo, Japan).

2.2. Protocol for the antimycobacterial activity screening (Microplate Alamar Blue Assay)

The Minimum Inhibitory Concentrations (MIC) of the synthesized compounds tested using \textit{in-vitro} MABA (Microplate Alamar Blue Assay) assay using the reported protocol\textsuperscript{36-38}. The \textit{Mycobacterium tuberculosis} H37Rv strain was used for the screening. The inoculum was prepared from fresh L J medium. Stock solutions of test compounds were made as 10 mM DMSO solution and further diluted in Middlebrook 7H9 broth at four-fold the final highest concentration tested was 100 µM. Serial dilution was performed for each compound in 96-well microtitre plates using 100 µl of Middlebrook 7H9 broth. The assay was performed in duplicate for each sample and the readings were compared to standard TB drug ethambutol. Sterile water was added to all perimeter wells to maintain the humidity during the incubation period of 7 days at 37 °C. After the incubation period, Alamar blue solution (30 µL) was added to each well and the plate was pre-incubated overnight. Bacterial growth was observed by a colour change from blue to pink and the minimum concentration that didn’t change the colour was taken as its MIC value.

2.3. Protocol for antiproliferative studies (MTT assay)
The cytotoxicity study was carried out as described previously [32, 33]. Briefly, 20×10³ of A549 and HeLa S3 cells/well were seeded in 96 well plates and incubated under humidified condition at 5% of CO₂ and 95% of air for 24 h. Then, cells were washed twice with PBS and incubated with serially diluted synthesized compounds (100 to 3.125 µM) in DMEM for 24 h. After 24 h treatment, cells were washed with PBS and MTT was added. After incubation of 3-4 h, 100 µL of DMSO was added and the result was measured at 570 nm. The cell viability was calculated by the following formula: Cell viability (%) = \[
\frac{\text{Abs (Test sample)} - \text{Abs (Blank)}}{\text{Abs (Control)} - \text{Abs (Blank)}} \times 100\%
\]

2.4. Fluorescence imaging

The 1×10⁵ of A549 cell line were seeded in 30 mm plate and incubated at 37 °C under 5% CO₂, 95% air for 24 h. After attachment of cells, washed twice with PBS and incubated with freshly prepared DMEM contained active compounds (4c and 4f). After 24 h incubation, 20 µL of EB/AO reagent was added (control and treated) and incubated for 10-15 min at dark condition. The cellular level changes were captured by fluorescence microscope (Biorevo, BZ-9000, Keyence) [34].

2.5. Colony formation studies

The A549 cell line (500 cells/well) were seeded in 24 well tissue culture plate and incubated under humidified condition. Next day, the cells were treated with active compounds such as 4c (5, 7.5 and 10 µM) and 4f (5, 10 and 20 µM) for 24 h. After 24 h treatment, media was removed and incubated with fresh DMEM for 10 days. After 10 days, wells were washed twice with PBS and incubated with crystal violet solution for 15 min. Then, each well washed with tap water and dried. The data was calculated by Image J software using colony area [35].

2.6. Crystallographic data of compound 4m and 4n
CCDC 1922304 and CCDC 1922969 contain the supplementary crystallographic data (.cif) of the compounds 4m and 4n respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

3.1. Spectral data

1'-((2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-benzoyl-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4a)

Color: white; M. P.: 188–190 °C; IR (KBr, cm⁻¹): 3434, 1720, 1681; ¹H NMR (400Hz, DMSO-d₆) δ: 1.82 (broad singlet, 4H), 2.36 (broad singlet, 2H), 4.21 (broad singlet, 1H), 4.57 (t, J = 11.2 Hz, 1H), 5.10 (d, J = 11.2 Hz, 1H), 6.43 (d, J = 6.4 Hz, 1H), 6.65 (s, 1H), 6.77 (s, 1H), 7.02 (s, 1H), 7.10 (s, 4H), 7.40 (s, 1H), 7.62-8.05 (m, 6H), 8.24 (d, J = 7.2 Hz, 1H), 8.35 (d, J = 7.2 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ: 195.81, 177.69, 147.57, 144.91, 144.71, 140.48, 138.88, 137.85, 134.70, 133.17, 130.66, 129.25, 128.64, 127.70, 126.03, 124.98, 124.67, 119.19, 112.41, 110.91, 78.85, 72.32, 71.53, 64.67, 46.76, 28.65, 26.86; ESI-MS: m/z 578 (M+1); Anal. Calcd. For C₃₆H₂₈N₆O₂: C, 74.98; H, 4.89; N, 14.57; Found: C, 74.73; H, 5.01; N, 14.71.

1'-((2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-(4-methylbenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4b)

Color: white; M. P.: 224–226 °C; IR (KBr, cm⁻¹): 3474, 1716, 1673; ¹H NMR (400 Hz, DMSO-d₆) δ: 1.68-1.81 (m, 4H), 2.21 (s, 3H), 2.36 (broad singlet, 2H), 4.18-4.24 (m, 1H), 4.58 (t, J = 11.2 Hz, 1H), 5.07 (d, J = 11.2 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 6.65 (d, J = 7.2 Hz, 1H), 6.77 (t, J = 7.2 Hz, 1H), 6.99-7.04 (m, 3H) 7.14 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.69-7.76 (m, 2H), 7.85 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 9.22 (s, 1H), 10.16 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ: 196.69, 179.14, 148.41, 145.65, 145.39, 143.78, 142.36,
1'(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-(4-ethylbenzoyl)-1',2',5',6',7',7a'-hexahydropiro[indoline-3,3'-pyrrolizin]-2-one, (4c)

Color: white; M. P.: 228–230 °C; IR (KBr, cm⁻¹): 3185, 1725, 1671; ¹H NMR (400 Hz, DMSO-d₆) δ: 1.06 (t, J = 8.0 Hz, 3H), 1.71-1.81 (m, 4H), 2.37 (s, 2H), 2.75 (q, J = 8.0 Hz, 2H), 4.18-4.23 (m, 1H), 4.58 (t, J = 11.2 Hz, 1H), 5.07 (d, J = 11.2 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H) 6.77 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 7.2 Hz, 3H), 7.17 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 8.0 Hz, 1H), 7.68-7.76 (m, 2H), 7.85 (t, J = 7.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.35 (d, J = 8.0 Hz, 1H), 9.22 (s, 1H), 10.17 (s, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ: 196.61, 179.16, 149.84, 148.40, 145.65, 145.39, 142.36, 139.46, 134.65, 133.97, 131.33, 129.68, 129.29, 128.71, 128.45, 128.33, 128.01, 126.51, 125.39, 124.91, 121.45, 119.89, 113.32, 110.15, 79.67, 72.98, 65.38, 47.64, 45.10, 29.35, 28.46, 27.30, 15.41; ESI-MS: m/z 606 (M+1); Anal. Calcd. For C₃₈H₃₂N₆O₂: C, 75.69; H, 5.63; N, 13.72.

1'-2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'--(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydropiro[indoline-3,3'-pyrrolizin]-2-one, (4d)

Color: white; M. P.: 213–215 °C; IR (KBr, cm⁻¹): 3271, 1736, 1675; ¹H NMR (400 Hz, DMSO-d₆) δ: 1.81 (broad singlet, 4H), 2.36 (m, 2H), 3.71 (s, 3H), 4.20 (broad singlet, 1H), 4.60 (t, J = 11.2 Hz, 1H), 5.05 (d, J = 11.2 Hz, 1H), 6.49 (d, J = 7.2 Hz, 1H), 6.66-6.78 (m, 4H), 7.02 (t, J = 7.2 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.59-7.86 (m, 4H), 7.95 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.2 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 9.21 (s, 1H),
10.17 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\): 195.14, 179.24, 163.40, 148.42, 145.66, 145.38, 142.32, 139.44, 133.97, 131.32, 130.56, 129.71, 129.30, 128.44, 126.52, 125.40, 124.96, 121.43, 119.92, 113.71, 113.35, 110.14, 73.13, 72.31, 65.12, 55.92, 47.61, 45.10, 29.41, 27.36; ESI-MS: \(m/z\) 608 (M+1); Anal. Calcd. For C\(_{37}\)H\(_{30}\)N\(_6\)O\(_3\): C, 73.25; H, 4.98; N, 13.85; Found: C, 73.04; H, 4.91; N, 13.99.

**1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-(4-fluorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4e)**

Color: white; M. P.: 196–198 °C; IR (KBr, cm\(^{-1}\)): 3455, 1710, 1682; \(^1\)H NMR (400 Hz, DMSO-\(d_6\)) \(\delta\): 1.68-1.80 (m, 4H), 2.36 (s, 2H), 4.17-4.22 (broad singlet, 1H), 4.56 (t, \(J = 10.8\) Hz, 1H), 6.46 (d, \(J = 7.6\) Hz, 1H), 6.64 (d, \(J = 7.2\) Hz, 1H) 6.78 (t, \(J = 7.2\) Hz, 1H), 7.03 (t, \(J = 8.8\) Hz, 3H), 7.26 (t, \(J = 6.8\) Hz, 2H), 7.62 (t, \(J = 7.6\) Hz, 1H), 7.69-7.78 (m, 2H), 7.86 (t, \(J = 8.0\) Hz, 1H), 7.96 (d, \(J = 8.4\) Hz, 1H), 8.05 (d, \(J = 8.4\) Hz, 1H), 8.23 (d, \(J = 8.0\) Hz, 1H), 8.34 (d, \(J = 8.4\) Hz, 1H), 9.23 (s, 1H), 10.14 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\): 196.38, 179.09, 148.39, 145.65, 145.40, 142.37, 139.63, 133.96, 133.71, 131.35, 130.99, 129.49, 129.34, 128.72, 128.45, 125.43, 124.78, 121.56, 119.92, 115.61, 113.27, 110.27, 79.67, 72.91, 65.80, 47.63, 44.86, 29.39, 27.33; ESI-MS: \(m/z\) 596 (M+1); Anal. Calcd. For C\(_{36}\)H\(_{27}\)FN\(_6\)O\(_2\): C, 72.71; H, 4.58; N, 14.13; Found: C, 72.46; H, 4.52; N, 14.30.

**1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-(4-chlorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4f)**

Color: white; M. P.: 237–239 °C; IR (KBr, cm\(^{-1}\)): 3174, 1725, 1676; \(^1\)H NMR (400 Hz, DMSO-\(d_6\)) \(\delta\): 1.67-1.80 (m, 4H), 2.36 (s, 2H), 4.17-4.21 (m, 1H), 4.56 (t, \(J = 11.2\) Hz, 1H), 5.10 (d, \(J = 11.2\) Hz, 1H), 6.47 (d, \(J = 7.6\) Hz, 1H), 6.63 (d, \(J = 7.6\) Hz, 1H) 6.78 (t, \(J = 7.2\) Hz, 1H), 7.04 (t, \(J = 7.2\) Hz, 1H), 7.17 (d, \(J = 8.0\) Hz, 2H), 7.27 (t, \(J = 7.6\) Hz, 2H), 7.62 (t, \(J
1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-(4-bromobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4g)

Color: white; M. P.: 243–245 °C; IR (KBr, cm\(^{-1}\)): 3174, 1724, 1676; \(^1\)H NMR (400 Hz, DMSO-\(d_6\)) \(\delta\): 1.68-1.80 (m, 4H), 2.36 (s, 2H), 4.16-4.20 (m, 1H), 4.55 (t, \(J = 11.2\) Hz, 1H), 5.09 (d, \(J = 11.2\) Hz, 1H), 6.47 (d, \(J = 7.6\) Hz, 1H), 6.63 (d, \(J = 7.6\) Hz, 1H), 6.78 (t, \(J = 7.2\) Hz, 1H), 7.03-7.11 (m, 3H), 7.41 (d, \(J = 7.6\) Hz, 2H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.68-7.78 (m, 2H), 7.87 (t, \(J = 7.6\) Hz, 1H), 7.96 (d, \(J = 8.0\) Hz, 1H), 8.05 (d, \(J = 8.4\) Hz, 1H), 8.22 (d, \(J = 8.0\) Hz, 1H), 8.34 (d, \(J = 8.4\) Hz, 1H), 9.22 (s, 1H), 10.18 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\): 196.96, 178.99, 148.38, 145.64, 145.41, 142.38, 139.66, 136.00, 133.96, 131.47, 129.98, 129.35, 128.73, 128.45, 127.49, 125.43, 124.72, 119.92, 113.35, 79.10, 72.85, 47.58, 44.82, 29.40, 27.33; ESI-MS: \(m/z\) 657 (M+2); Anal. Calcd. For C\(_{36}\)H\(_{27}\)BrN\(_6\)O\(_2\): C, 65.96; H, 4.15; N, 12.82; Found: C, 65.76; H, 4.08; N, 12.95.

1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-benzoyl-5-chloro-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4h)

Color: white; M. P.: 192–194 °C; IR (KBr, cm\(^{-1}\)): 3402, 1721, 1679; \(^1\)H NMR (400 Hz, DMSO-\(d_6\)) \(\delta\): 1.75-1.86 (m, 4H), 2.31-2.42 (m, 2H), 4.16-4.22 (m, 1H), 4.48 (t, \(J = 11.2\) Hz, 1H), 5.16 (d, \(J = 11.2\) Hz, 1H), 6.46 (d, \(J = 8.4\) Hz, 1H), 6.61 (s, 1H), 7.09-2.27 (m, 5H), 7.44 (t, \(J = 7.2\) Hz, 1H), 7.61 (t, \(J = 7.6\) Hz, 1H), 7.69-7.77 (m, 3H), 7.86 (t, \(J = 8.0\) Hz, 1H), 7.96
(d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 9.26 (s, 1H), 10.28 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_{6}\)) \(\delta\): 197.35, 178.58, 148.41, 145.68, 145.46, 141.30, 139.54, 136.77, 133.96, 133.69, 131.38, 129.38, 129.16, 128.76, 128.49, 128.14, 126.94, 125.64, 125.42, 119.95, 113.19, 79.67, 73.06, 65.32, 47.51, 44.96, 29.35, 27.56; ESI-MS: m/z 612 (M+1); Anal. Calcd. For C\(_{36}\)H\(_{27}\)ClN\(_{6}\)O\(_{2}\): C, 70.76; H, 4.45; N, 13.75; Found: C, 70.52; H, 4.56; N, 13.93.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-chloro-2’-(4-methylbenzoyl)-1’,2’,5’,6’,7’,7a’-hexahydrospiro[indoline-3,3’-pyrrolizin]-2-one, (4i)

Color: white; M. P.: 216–218 °C; IR (KBr, \text{cm}^{-1}): 3402, 1720, 1673; \(^1\)H NMR (400 Hz, DMSO-d\(_{6}\)) \(\delta\): 1.85 (Broad singlet, 4H), 2.26 (s, 3H), 2.40 (s, 2H), 4.22-4.28 (m, 1H), 4.62 (t, J = 11.2 Hz, 1H), 5.12 (d, J = 11.2 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.70 (d, J = 7.2 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.2 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 7.64-7.81 (m, 3H), 7.90 (t, J = 7.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 9.26 (s, 1H), 10.21 (s, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_{6}\)) \(\delta\): 197.36, 179.82, 149.08, 146.32, 146.07, 144.45, 143.03, 140.14, 135.14, 134.56, 132.01, 130.34, 129.74, 129.13, 128.91, 127.12, 126.08, 125.56, 114.01, 110.85, 76.67, 73.64, 66.05, 48.31, 45.70, 30.03, 27.98, 22.19; ESI-MS: m/z 626 (M+1); Anal. Calcd. For C\(_{37}\)H\(_{29}\)ClN\(_{6}\)O\(_{2}\): C, 71.09; H, 4.68; N, 13.44; Found: C, 71.35; H, 4.77; N, 13.27.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-chloro-2’-(4-ethylbenzoyl)-1’,2’,5’,6’,7’,7a’-hexahydrospiro[indoline-3,3’-pyrrolizin]-2-one, (4j)

Color: white; M. P.: 221–223 °C; \(^1\)H NMR (400 Hz, DMSO-d\(_{6}\)) \(\delta\): 1.08 (t, J = 8.0 Hz, 3H, CH\(_3\)), 1.70-1.92 (m, 4H), 2.42 (s, 2H), 2.52 (s, 2H), 4.22-4.27 (m, 1H), 4.63 (t, J = 11.2 Hz, 1H), 5.06 (d, J = 11.2 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H) 6.76 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.66-
7.73 (m, 2H), 7.83 (t, J = 7.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 8.01 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 9.17 (s, 1H), 10.12 (s, 1H); 13C NMR (100 MHz, DMSO-d$_6$) δ: 197.10, 179.65, 150.33, 148.89, 146.14, 145.88, 142.84, 139.95, 135.13, 134.46, 131.82, 130.16, 129.78, 129.20, 128.93, 128.50, 126.99, 125.88, 125.39, 121.94, 120.37, 113.80, 110.64, 80.16, 73.47, 65.86, 48.13, 45.59, 29.84, 28.95, 27.78, 15.90.

Anal. Calcd. For C$_{38}$H$_{31}$ClN$_6$O$_2$: C, 71.41; H, 4.89; N, 13.15; Found: C, 71.22; H, 4.82; N, 13.36.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-chloro-2’-(4-methoxybenzoyl)-1’,2’,5’,6’,7’,7a’-hexahydrospiro[indoline-3,3’-pyrrolizin]-2-one, (4k)

Color: white; M. P.: 236–238 °C; IR (KBr, cm$^{-1}$): 3252, 1738, 1675; 1H NMR (400 Hz, DMSO-d$_6$) δ: 1.79 (broad singlet, 4H), 2.31-2.40 (m, 2H), 3.72 (s, 3H), 4.19 (broad singlet, 1H), 4.49 (t, J = 11.2 Hz, 1H), 5.10 (d, J = 11.2 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.63 (s, 1H), 6.75 (d, J = 8.0 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.69-7.79 (m, 2H), 7.86 (t, J = 7.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 9.24 (s, 1H), 10.24 (s, 1H); 13C NMR (100 MHz, DMSO-d$_6$) δ: 194.91, 178.71, 163.63, 148.41, 145.67, 145.44, 141.26, 139.44, 133.94, 131.39, 130.71, 129.59, 129.37, 129.23, 128.78, 128.44, 127.06, 125.56, 125.40, 119.94, 113.91, 113.16, 79.67, 73.34, 64.68, 55.88, 47.51, 45.12, 29.43, 27.67; ESI-MS: m/z 642 (M+1); Anal. Calcd. For C$_{37}$H$_{29}$ClN$_6$O$_3$: C, 69.32; H, 4.56; N, 13.11; Found: C, 69.58; H, 4.62; N, 12.94.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-chloro-2’-(4-fluorobenzoyl)-1’,2’,5’,6’,7’,7a’-hexahydrospiro[indoline-3,3’-pyrrolizin]-2-one, (4l)

Color: white; M. P.: 204–206 °C; IR (KBr, cm$^{-1}$): 3412, 1722, 1680; 1H NMR (400 Hz, DMSO-d$_6$) δ: 1.78 (broad singlet, 4H), 2.32 (s, 1H), 2.40 (s, 1H), 4.17 (broad singlet, 1H),
4.46 (t, $J = 11.6$ Hz, 1H), 5.16 (d, $J = 11.6$ Hz, 1H), 6.48 (d, $J = 8.4$ Hz, 1H), 6.60 (s, 1H) 7.05-7.13 (m, 3H), 7.34 (s, 1H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.69-7.89 (m, 3H), 7.87 (t, $J = 7.2$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 8.34 (d, $J = 8.4$ Hz, 1H), 9.23 (s, 1H), 10.14 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ: 197.31, 180.02, 149.32, 146.58, 146.34, 143.31, 140.56, 134.89, 134.64, 132.28, 131.92, 130.43, 130.27, 129.65, 129.38, 126.36, 125.71, 122.49, 120.85, 116.54, 114.20, 111.20, 73.46, 66.74, 48.56, 45.79, 30.33, 28.26; Anal. Calcd. For C$_{36}$H$_{26}$ClFN$_6$O$_2$: C, 68.73; H, 4.17; N, 13.36; Found: C, 68.96; H, 4.09; N, 13.52.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-chloro-2’-(4-chlorobenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4m)

Color: white; M. P.: 201–203 °C; IR (KBr, cm$^{-1}$): 3423, 1729, 1673; $^1$H NMR (400 Hz, DMSO-d$_6$) δ: 1.78 (Broad singlet, 4H), 2.31 (s, 1H), 2.40 (s, 1H), 4.18 (Broad singlet, 1H), 4.55 (t, $J = 10.8$ Hz, 1H), 5.16 (d, $J = 11.6$ Hz, 1H), 6.49 (d, $J = 7.6$ Hz, 1H), 6.59 (s, 1H), 7.13 (d, $J = 8.4$ Hz, 1H) 7.24-7.33 (m, 4H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.69-7.78 (s, 2H), 7.87 (t, $J = 7.2$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.33 (d, $J = 8.4$ Hz, 1H), 9.25 (s, 1H), 10.30 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ: 196.57, 178.44, 148.32, 145.67, 145.47, 141.24, 139.63, 138.61, 135.46, 133.93, 131.42, 130.01, 129.40, 128.46, 126.79, 125.74, 125.42, 119.94, 113.16, 111.67, 79.61, 73.08, 72.29, 65.42, 47.51, 29.40, 27.62; ESI-MS: m/z 646 (M+1); Anal. Calcd. For C$_{36}$H$_{26}$ClFN$_6$O$_2$: C, 66.98; H, 4.06; N, 13.02; Found: C, 66.72; H, 4.11; N, 13.17.

1’-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2’-(4-bromobenzoyl)-5-chloro-1’,2’,5’,6’,7’,7a’-hexahydrospiro[indoline-3,3’-pyrrolizin]-2-one, (4n)

Color: white; M. P.: 235–237 °C; IR (KBr, cm$^{-1}$): 3448, 1727, 1671; $^1$H NMR (400 Hz, DMSO-d$_6$) δ: 1.76 (Broad singlet, 4H), 2.30 (s, 1H), 2.39 (s, 1H), 4.19 (Broad singlet, 1H),
4.55 (t, J = 11.2 Hz, 1H), 5.15 (d, J = 11.2 Hz, 1H), 6.49 (d, J = 8.4 Hz, 1H), 6.59 (s, 1H), 7.12-7.18 (m, 3H), 7.45 (d, J = 7.6 Hz, 2H) 7.61 (t, J = 7.2 Hz, 1H), 7.69-7.78 (m, 2H), 7.87 (t, J = 7.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H), 9.22 (s, 1H), 10.18 (s, 1H); 13C NMR (100 MHz, DMSO-d6) δ: 196.78, 178.45, 148.38, 145.67, 145.47, 141.26, 139.65, 135.78, 133.94, 131.63, 131.42, 130.12, 129.42, 128.95, 128.53, 127.87, 126.80, 125.73, 125.44, 119.94, 113.18, 73.08, 72.22, 65.38, 47.50, 44.82, 29.41, 27.63; ESI-MS: m/z 691 (M+2); Anal. Calcd. For C36H26BrClN6O2: C, 62.67; H, 3.80; N, 12.18; Found: C, 62.86; H, 3.88; N, 12.04.

1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-2'-benzoyl-5-bromo-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4o)

Color: white; M. P.: 218–220 °C; IR (KBr, cm⁻¹): 3203, 1723, 1679; ¹H NMR (400 Hz, DMSO-d6) δ: 1.81 (broad singlet, 4H), 2.28-2.39 (m, 2H), 4.20 (broad singlet, 1H), 4.44 (t, J = 10.4 Hz, 1H), 5.15 (d, J = 12.0 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 6.73 (s, 1H), 7.20-2.26 (m, 5H), 7.44 (t, J = 6.4 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.70-7.76 (m, 2H), 7.87 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 9.26 (s, 1H), 10.29 (s, 1H); ¹³C NMR (100 MHz, DMSO-d6) δ: 197.43, 178.43, 148.43, 145.67, 141.67, 139.54, 136.78, 133.96, 133.66, 132.69, 131.39, 129.39, 129.18, 128.77, 128.51, 128.10, 127.35, 125.39, 119.98, 113.14, 111.99, 73.04, 73.02, 65.32, 47.55, 44.94, 29.32, 27.54; ESI-MS: m/z 657 (M+1); Anal. Calcd. For C36H27BrN6O2: C, 65.96; H, 4.15; N, 12.82; Found: C, 65.73; H, 4.22; N, 12.99.

1'-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-5-bromo-2'-(4-methoxybenzoyl)-1',2',5',6',7',7a'-hexahydrospiro[indoline-3,3'-pyrrolizin]-2-one, (4p)

Color: white; M. P.: 232–234 °C; IR (KBr, cm⁻¹): 3248, 1738, 1675; ¹H NMR (400 Hz, DMSO-d6) δ: 1.79 (broad singlet, 4H), 2.37 (s, 2H), 3.71 (s, 3H), 4.18 (s, 1H), 4.46 (s, 1H),
5.09 (s, 1H), 6.46 (s, 1H), 6.75 (s, 2H) 7.23-8.34 (m, 12H), 9.23 (s, 1H), 10.33 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 194.86, 178.40, 148.45, 145.71, 145.48, 141.71, 139.46, 133.99, 132.44, 131.37, 130.70, 130.60, 129.35, 128.44, 125.40, 125.29, 124.47, 123.14, 119.96, 113.86, 113.36, 113.05, 112.09, 79.56, 73.28, 64.66, 55.94, 48.53, 45.16, 27.74, 21.53; ESI-MS; m/z 687 (M+1); Anal. Calcd. For C$_{37}$H$_{29}$BrN$_6$O$_3$: C, 64.82; H, 4.26; N, 12.26; Found: C, 64.60; H, 4.17; N, 12.44.

3.2. Copies of the characterization spectra ($^1$H-NMR, $^{13}$C-NMR, mass and IR spectra) of the synthesized compounds 4a-p.

$^1$H NMR Spectrum of compound 4a
$^{13}$C NMR Spectrum of compound 4a

Mass spectrum of compound 4a
IR Spectrum of compound 4a

^1H NMR Spectrum of compound 4b
$^{13}$C NMR Spectrum of compound 4b

Mass spectrum of compound 4b
IR Spectrum of compound 4b

\[ \text{IR Spectrum} \]

\[ \text{N} \]
\[ \text{H} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{C} \]
\[ \text{H} \]
\[ \text{3} \]

\[ \text{H NMR Spectrum of compound 4c} \]

\[ \text{H NMR Spectrum} \]

\[ \text{N} \]
\[ \text{H} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{N} \]
\[ \text{N} \]
\[ \text{C} \]
\[ \text{H} \]
\[ \text{3} \]
$^{13}$C NMR Spectrum of compound 4c

Mass spectrum of compound 4c
IR Spectrum of compound 4c

\[ \text{IR Spectrum} \]

$\text{1H NMR Spectrum of compound 4d}$

\[ \text{1H NMR Spectrum} \]
$^{13}$C NMR Spectrum of compound 4d

Mass spectrum of compound 4d
IR Spectrum of compound 4d

1H NMR Spectrum of compound 4e
$^{13}$C NMR Spectrum of compound 4e

Mass spectrum of compound 4e
IR Spectrum of compound 4e

^1H NMR Spectrum of compound 4f
$^{13}$C NMR Spectrum of compound 4f

Mass spectrum of compound 4f
IR Spectrum of compound 4f

H NMR Spectrum of compound 4g
\[ ^{13}C \text{ NMR Spectrum of compound 4g} \]

[Image of NMR spectrum]

\[ \text{Mass spectrum of compound 4g} \]

[Image of Mass spectrum]
IR Spectrum of compound 4g

\[ \text{IR Spectrum} \]

$^1$H NMR Spectrum of compound 4h

\[ \text{NMR Spectrum} \]
$^{13}$C NMR Spectrum of compound 4h

IR Spectrum of compound 4h
$^1$H NMR Spectrum of compound 4i

$^{13}$C NMR Spectrum of compound 4i
IR Spectrum of compound 4i

Mass spectrum of compound 4i
$^1$H NMR Spectrum of compound 4j

$^{13}$C NMR Spectrum of compound 4j
$^1$H NMR Spectrum of compound 4k

$^{13}$C NMR Spectrum of compound 4k
IR Spectrum of compound 4k

Mass spectrum of compound 4k
$^1$H NMR Spectrum of compound 4l

$^{13}$C NMR Spectrum of compound 4l
IR Spectrum of compound 4l

1H NMR Spectrum of compound 4m
$^{13}$C NMR Spectrum of compound 4m

IR Spectrum of compound 4m
Mass spectrum of compound 4m

$^1$H NMR Spectrum of compound 4n
$^{13}$C NMR Spectrum of compound 4n

IR Spectrum of compound 4n
Mass spectrum of compound 4n

1H NMR Spectrum of compound 4o
$^{13}$C NMR Spectrum of compound 4o

IR Spectrum of compound 4o
Mass spectrum of compound 4o

1H NMR Spectrum of compound 4p
$^{13}$C NMR Spectrum of compound 4p

Mass spectrum of compound 4p
4.1. Spectral data for the compounds 1a-g.

3-(2-[(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl]-1-phenylprop-2-en-1-one (1a)

Color: white; Yield: 80%. Reaction time: 80 min. M.P. 206–208 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 7.62 (s, 3H), 7.71-7.77 (m, 2H), 7.84 (s, 1H), 7.96 (d, $J$ = 15.2 Hz, 2H), 8.13-8.20 (m, 4H), 8.25 (d, $J$ = 6.8 Hz, 2H), 8.30 (d, $J$ = 8.0 Hz, 1H), 9.50 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 189.51, 147.47, 146.69, 145.76, 139.82, 139.41, 137.67, 133.93, 133.24, 132.69, 129.70, 129.35, 129.14, 128.94, 128.89, 127.81, 125.89, 124.23, 120.02, 113.93.

3-(2-[(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl]-1-(p-tolyl)prop-2-en-1-one (1b)

Color: white; Yield: 75%. Reaction time: 90 min. M.P. 189–191 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$: 2.43 (s, 3H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.59 (t, $J$ = 8.0 Hz, 1H), 7.73 (t, $J$ = 8.0 Hz, 1H), 7.79 (t, $J$ = 7.2 Hz, 1H), 7.93-7.99 (m, 2H), 8.08-8.14 (m, 3H), 8.21-8.25 (m, 4H), 9.44 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$: 188.81, 147.45, 146.66, 145.75, 144.47,
3-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-1-(4-ethylphenyl)prop-2-en-1-one (1c)
Color: white; Yield: 74%. Reaction time: 86 min. M.P. 170–172 °C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 1.24 (t, \(J = 7.6\) Hz, 3H), 2.72 (d, \(J = 7.6\) Hz, 2H), 7.26 (d, \(J = 8.0\) Hz, 1H), 7.44 (d, \(J = 8.0\) Hz, 1H), 7.62 (t, \(J = 7.6\) Hz, 1H), 7.74-7.85 (m, 3H), 7.91-8.00 (m, 2H), 8.11-8.16 (m, 3H), 8.24 (d, \(J = 7.6\) Hz, 2H), 8.29 (d, \(J = 8.0\) Hz, 1H), 9.49 (s, 1H); \(^1^3\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 188.89, 150.48, 147.46, 146.67, 145.75, 139.76, 138.95, 136.60, 135.43, 133.26, 132.66, 129.70, 129.39, 129.09, 128.94, 128.88, 128.75, 128.54, 128.42, 127.84, 125.89, 124.32, 120.02, 113.89, 28.72, 15.65.

3-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1d)
Color: yellow; Yield: 76%. Reaction time: 82 min. M.P. 195–197 °C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 3.90 (s, 3H), 7.10 (d, \(J = 8.0\) Hz, 2H), 7.60 (t, \(J = 7.6\) Hz, 1H), 7.74 (t, \(J = 7.2\) Hz, 1H), 7.81 (t, \(J = 6.8\) Hz, 1H), 7.90-7.98 (m, 3H), 8.12-8.23 (m, 6H), 9.46 (s, 1H); \(^1^3\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 187.50, 163.96, 147.45, 146.64, 145.74, 139.67, 138.34, 133.27, 132.60, 131.57, 130.55, 129.69, 127.86, 125.86, 124.44, 120.02, 114.61, 113.84, 56.12.

3-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-1-(4-fluorophenyl)prop-2-en-1-one (1e)
Color: white; Yield: 79%. Reaction time: 78 min. M.P. 244–246 °C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 7.67 (d, \(J = 6.0\) Hz, 1H), 7.79-7.89 (m, 4H), 8.01-8.10 (m, 2H), 8.16-8.33 (m, 7H) 9.52 (s, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)+ DMSO-d\(_6\)) \(\delta\): 188.87, 146.43, 140.40,
3-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-1-(4-chlorophenyl)prop-2-en-1-one (1f)

Color: white; Yield: 86%. Reaction time: 60 min. M.P. 214–216 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) δ: 7.59-7.66 (m, 3H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.84 (t, $J = 7.6$ Hz, 1H), 7.96 (d, $J = 6.0$ Hz, 1H), 8.00 (s, 1H), 8.11-8.16 (m, 2H), 8.19-8.26 (m, 5H), 9.47 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$+ DMSO-d$_6$) δ: 188.26, 145.81, 139.79, 138.96, 132.50, 130.92, 129.49, 129.31, 128.99, 128.65, 127.72, 125.69, 125.39, 124.01, 123.02, 119.95, 113.88.

3-(2-(1H-benzo[d][1,2,3]triazol-1-yl)quinolin-3-yl)-1-(4-bromophenyl)prop-2-en-1-one (1g)

Color: yellow; Yield: 84%. Reaction time: 65 min. M.P. 209–211 °C; $^1$H NMR (400 MHz, DMSO-d$_6$) δ: 7.60 (d, $J = 6.0$ Hz, 1H), 7.72-7.82 (m, 3H), 7.94-8.03 (m, 2H), 8.09-8.26 (m, 8H) 9.43 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ: 189.19, 146.74, 140.72, 139.89, 133.43, 131.85, 130.42, 130.24, 129.92, 129.58, 128.65, 126.62, 126.32, 124.94, 123.95, 120.88, 114.81.

4.2. Spectrums of compounds 1a-g.
$^1$H NMR Spectrum of compound 1a

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

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

$^{13}$C NMR Spectrum of compound 1c
$^1$H NMR Spectrum of compound 1d

$^{13}$C NMR Spectrum of compound 1d
$^{13}$C NMR Spectrum of compound 1f
$^1$H NMR Spectrum of compound 1g

$^{13}$C NMR Spectrum of compound 1g