Sustainable Copper Nanocomposite for Multicomponent Synthesis of Triazolo Quinolines and Triazolyl Benzamide Derivatives and Their Bioactivity Study

Nandini R.,[a] Byresh B. Kempegowda,[b] Sudhanva M. Srinivasa,[b] Umesh A. Kshirsagar,[c] Jan Grzegorz Malecki,[d] Siddappa A. Patil,[a] Shoyebmohamad F. Shaikh,[e] Manoj V. Mane, [a]* Ramesh B. Dateer [a]*

[a]Centre for Nano and Material Sciences, Jain Global Campus, JAIN (Deemed-to-be University), Bangalore - 562112, Karnataka, India.

[b]Adichunchanagiri Institute for Molecular Medicine, Adichunchanagiri Institute of Medical Sciences, Adichunchanagiri University, BG Nagara - 571448, Karnataka, India.

[c]Indian Institute of Technology, Indore - 453552, Madhya Pradesh, India.

[d]Institute of Chemistry, University of Silesia, 9th Szkolna Street, Katowice40-006, Poland.

[e]Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

*Corresponding authors, Email: d.ramesh@jainuniversity.ac.in; manoj.mane@jainuniversity.ac.in

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1. General considerations

Unless otherwise specified, The presence of different functional groups in Cu@PANI@Fe_3O_4 nanocomposite was analysed by Fourier Transform Infrared Spectroscopy (FT-IR) in a Perkin Elmer FT-IR instrument by KBr pellets method in the range of 4000 to 500 cm^{-1}. The crystallographic nature and the phase of the Cu@PANI@Fe_3O_4 nanocomposite were as examined and confirmed using powder X-ray diffraction spectroscopy (XRD) noted on a Rigaku X-Ray Diffraction Ultima IV (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan rate of 2º min^{-1} and theta value range of 10-80° at 30 kV voltage and 15 mA current. The surface area analysis of Cu@PANI@Fe_3O_4 nanocomposite was performed using Brunauer Emmet and Teller (BET) method on Belsorp-Max (M/s. Microtrac BEL, Japan) under an N_2 atmosphere at a temperature of -196 ºC. The corresponding pore size distribution of the catalyst was analyzed using Barrett Joyner Halenda's (BJH) method. The catalysts were degassed at 120 ºC for 4 h under vacuum before analysis to push out absorbed moisture. The thermal degradation of Cu@PANI@Fe_3O_4 nanocomposite was determined by a thermal analyzer within the temperature window of 27 ºC to 900 ºC under continuous N_2 flow with a heating rate of 5 ºC min^{-1}. The morphology and structural identity of Cu@PANI@Fe_3O_4 nanocomposite were investigated using a Field Emission Scanning Electron Microscope (JEOL JSM-7100F, Singapore) coupled with energy dispersive X-ray spectroscopy (EDX). The carbon tape on the aluminium metal stub was adequately covered with the powdered sample and subjected to sputtering using gold nanoparticles. All reactions were performed in completely dried glass wares if otherwise specified. All reagents were directly used as purchased without further purification unless otherwise specified. Column chromatography was performed using silica gel (60-120 mesh) and a proper eluent. Chemical shifts were expressed in parts per million (ppm) concerning the solvent peak (DMSO in DMSO-d6: 2.5 and 3.5 ppm). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Broadband proton decoupling was used to fully decouple ^{13}C {^1H} NMR and recorded on an Agilent

Technologies DD2 (100 MHz). Chemical changes were measured in parts per million (ppm) and compared to the center of a triplet at 44.0 parts per million (ppm) of DMSO-d6.

2. Synthesis of Cu@PANI@Fe_3O_4 nanocomposite

2.1 Synthesis of PANI@Fe_3O_4

Fe_3O_4 NPs were synthesized as per the reported procedure.[S1 -S3] Under ultrasonification, 0.1 g of Fe_3O_4 particles were completely disseminated in 100 mL of aqueous solution. The reaction system was subjected to intense agitation while submerged in an ice-water bath. Later on, HCl (0.1 M), polyaniline (PANI) and $K_2S_2O_8$ were successively added to the Fe_3O_4 dispersed solution in equal molar amounts. Then the reaction system was stirred at 0 °C for 5 hours. The black precipitate was then gathered and ultrasonically cleaned using ethanol and water through magnetic separation and dried at 80 °C for 12 hours.

2.2 Synthesis of Cu@PANI@Fe_3O_4 nanocomposite

The prepared PANI@Fe_3O_4 (100 mg) was ultrasonically dispersed in a solution containing $Cu(NO_3)_2$ (2 mmol), hydrazine hydrate (1 mL) and ethanol (10 mL).[S4] Later on, this reaction mixture is continued for sonication up to 3 hours followed by centrifugation (3x30 mL ethanol) and dried at 80 ºC for 12 h to obtain the required nanocomposite.

2.3 Characterization of Cu@PANI@Fe_3O_4 nanocomposite

2.3.1 Field Emission Scanning Electron Microscopic (FE-SEM) Analysis

FESEM analysis was carried out to know the surface morphology of the synthesized nanocomposite. The SEM images provided evidence that the Cu@PANI@Fe_3O_4 nanocomposite particles possessed agglomerated spherical morphology (Figure S1).

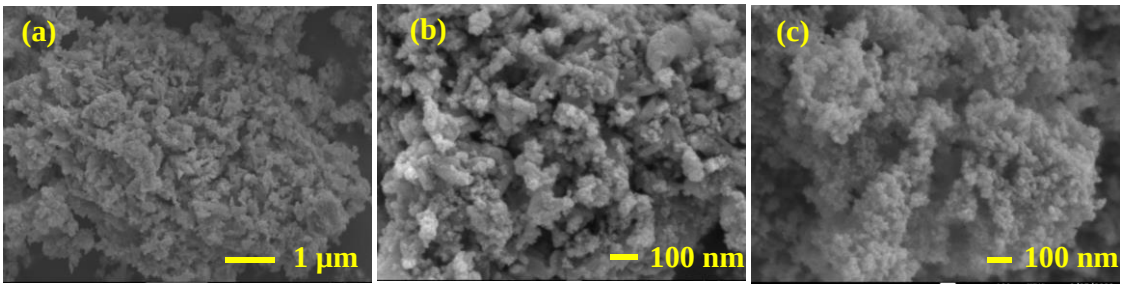


Figure S1. FESEM images of (a) Fe_3O_4 NPs (b) PANI@Fe_3O_4 and (c) Cu@PANI@Fe_3O_4 nanocomposite

2.3.2 Energy dispersive X-ray (EDX) analysis

The chemical composition of Cu@PANI@Fe_3O_4 nanocomposite was confirmed by EDX analysis which exhibited the characteristic peaks of Cu, O, Fe, C and N present in the nanocomposite (Figure S2). Further, elemental mapping confirms the uniform distribution of the Cu(0) NPs on the surface of the magnetite.

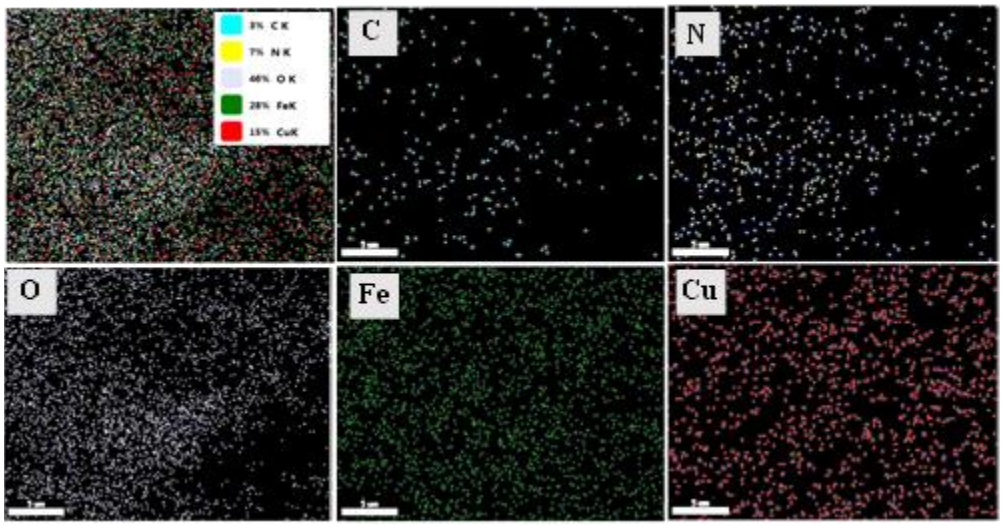


Figure S2. Energy Dispersive X-ray (EDX) Analysis of Cu@PANI@Fe_3O_4 nanocomposite

2.3.3 TG-DT Analysis

The thermal stability of the synthesized Cu@PANI@Fe_3O_4 nanocomposite was analyzed using Thermo Gravimetric (TG) and Differential Thermal (DT) Analysis (Figure S3). According to the data, the initial 5 % at around 200 ºC drop was observed due to moisture and ethanol evaporation from the nanocomposite and the later 10% loss at 360 ºC was due to the carbonization of the polymer shell (polyaniline) present in the nanocomposite. Further, the nanocomposite was found to be stable up to 800 ºC without any loss which in turn indicates the thermal stability even at higher temperatures. The DTA graph revealed the maximum weight loss occurred at 264.8 – 546.6 ºC which confirms the sustainability of Cu@PANI@Fe_3O_4 nanocomposite even at higher temperatures.

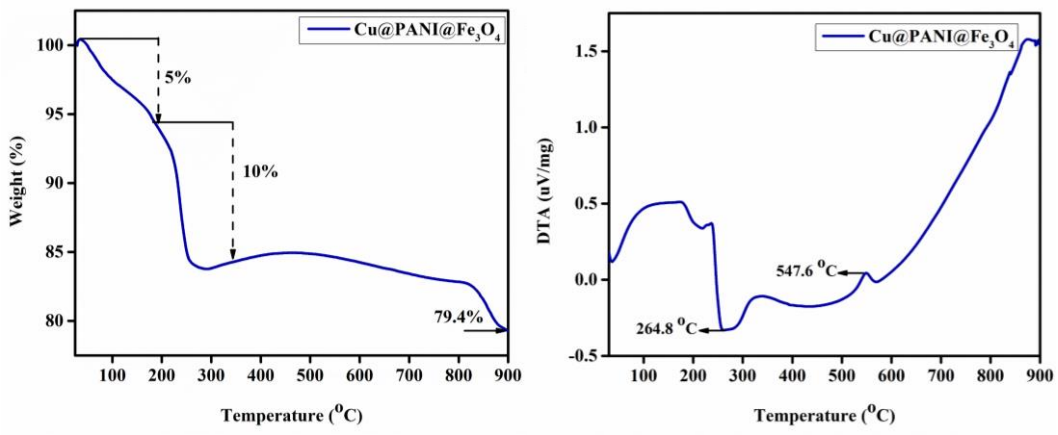


Figure S3. Thermo Gravimetric (TG) and Differential Thermal (DT) Analysis of Cu@PANI@Fe_3O_4 nanocomposite

2.3.4 BET-BJH Analysis

The surface area of the synthesized nanocomposite was analyzed using the nitrogen adsorption-desorption technique wherein this analysis suggest that it follows type III isotherm with mesoporous nature. The surface area of the nanocomposite was found to be 11.086 $m^2\ g^{-1}$ with a pore diameter of 18.57 nm and pore volume was found to be 0.0836 $cm^3\ g^{-1}$ (Figure S4).

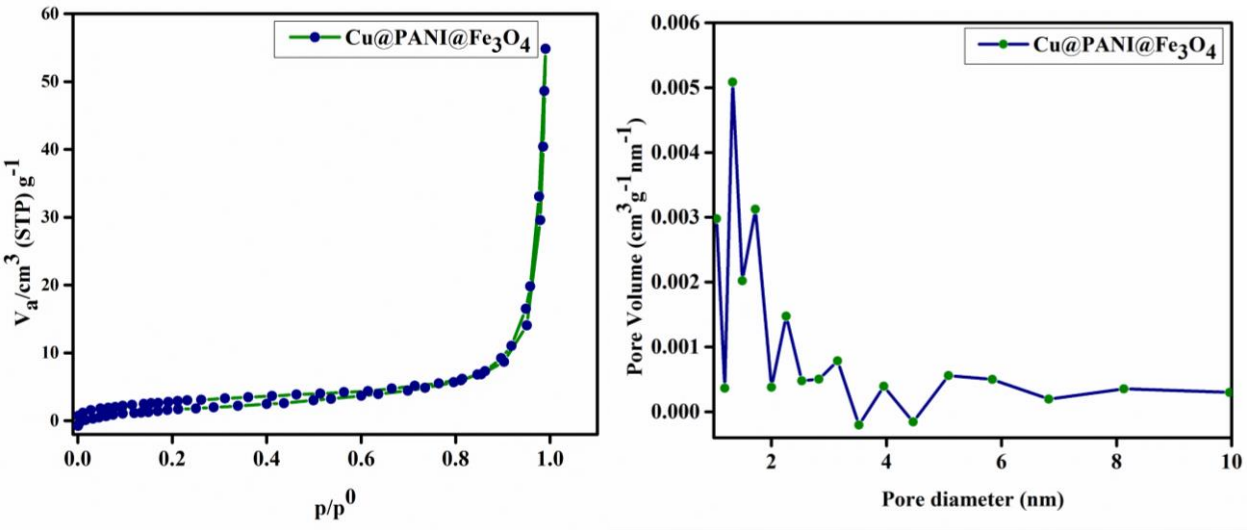


Figure S4. BET and BJH Analysis of Cu@PANI@Fe_3O_4 nanocomposite

2.3.5 Vibrating Sample Magnetometer (VSM) Analysis

A vibrating sample magnetometer (VSM) under 12,000 to 12,000 Oe at room temperature was used to investigate the magnetic characteristics of Cu@PANI@Fe_3O_4 nanocomposite, as illustrated in Figure S5. The undetectable coercivity force of the nanoparticles was determined using magnetization hysteresis loops, confirming their superparamagnetic nature. The saturation magnetization (M_s) of the synthesized nanocomposite was found to be 20.12 emu/g. The low M_s value was observed due to the covering of the polymer core around the core Fe_3O_4 NPs. Magnetic separability of the nanocomposite is well demonstrated wherein the nanocomposite suspended in ethanol was attracted towards the external bar magnet placed across the glass indicating easy separation of the nanocomposite.

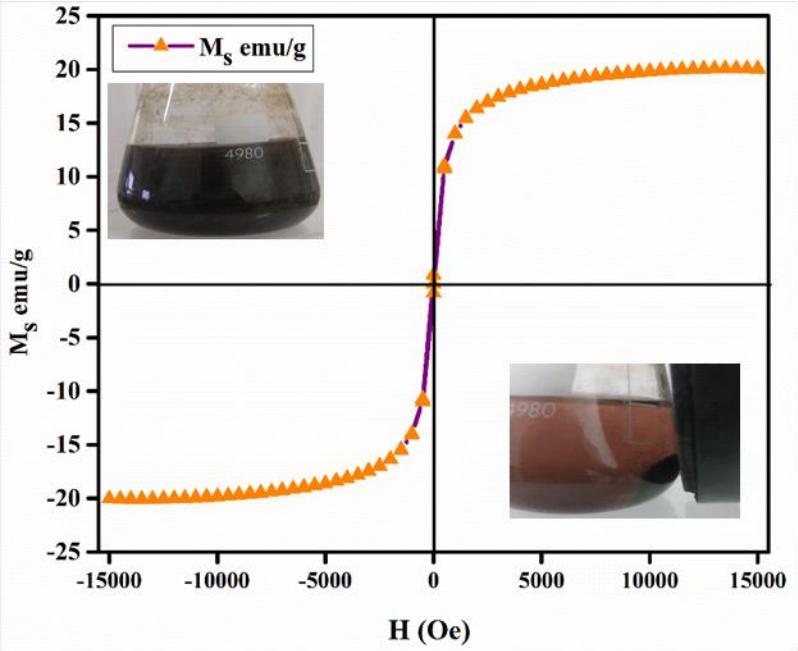
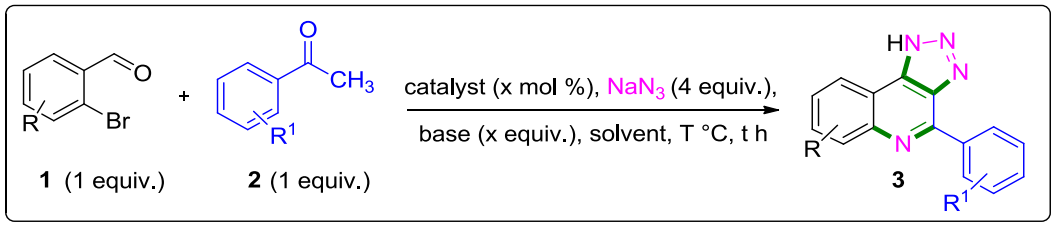
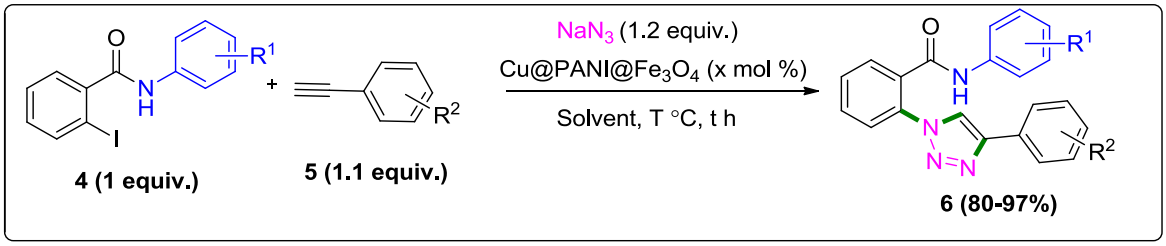


Figure S5. VSM analysis of Cu@PANI@Fe_3O_4 nanocomposite. The inset images demonstrate the magnetic separability using an external magnet

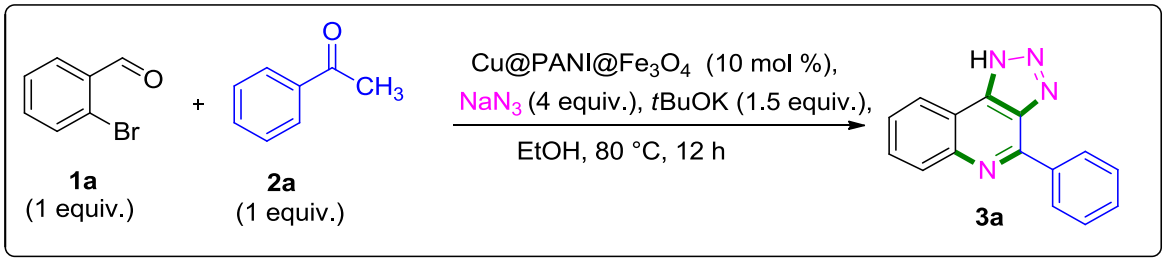
3. General experimental procedure for the optimization study of triazolo quinoline and triazolyl benzamide derivatives.



Initially, the Cu@PANI@Fe_3O_4 nanocomposite (Cu content, w/w: 29.61%, 0-20 mol%) and base (0-1.5 equiv.), was taken in an oven-dried 10 mL sealed tube. Later, 2-bromo benzaldehyde (1equiv.) acetophenone (1 equiv.) and sodium azide (NaN_3, 4 equiv.) along with the solvent (2 mL) was added to the same sealed tube and the reaction mixture was stirred at 60-120 ºC for 12-30 h. After the completion of the reaction (monitored by TLC), the catalyst was separated from the reaction mixture using an external magnet. Further, the crude compound was extracted using ethyl acetate (EtOAc) and brine solution (10 x 3). Then the organic layer was collected and evaporated using a rota evaporator to obtain the crude compound **3** (**a - i**). The crude compound was purified by column chromatography (eluent: 3-10% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield (by an average of two runs). A similar procedure was followed in the absence of a base to synthesize triazolyl benzamide derivatives **6 (a – l)**. The crude compound was purified by column chromatography (eluent: 3-10% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield (by an average of two runs).

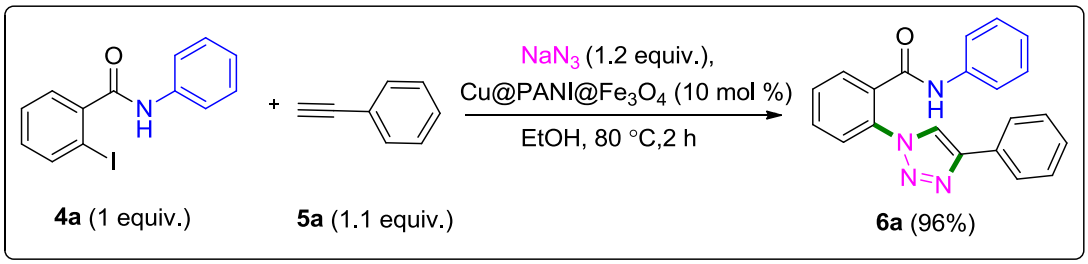


4. Exact experimental procedure for the synthesis of 1*H*-[1,2,3]triazolo[4,5-c]quinoline (3a) and *N*-(p-tolyl)-2-(1*H*-1,2,3-triazol-4-yl)benzamide (6a)

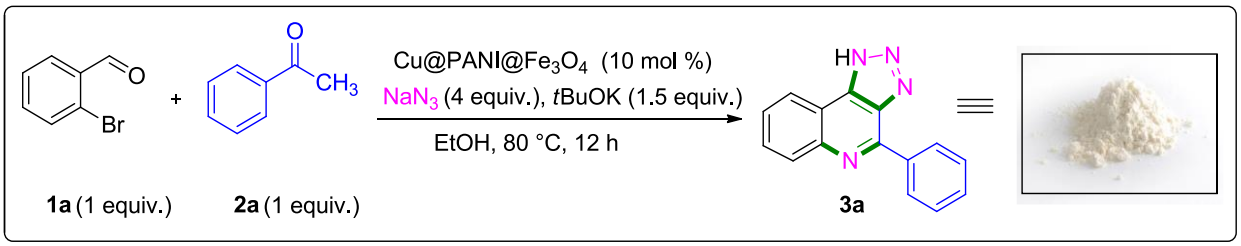


In an oven tried 10 mL sealed tube containing 10 mol % of Cu@PANI@Fe_3O_4 (Cu content, w/w: 29%) nanocomposite, Cs_2CO_3 (1.2 mmol) as a base was added 2-bromo benzaldehyde **1a** (0.5 mmol), acetophenone **2a** (0.6 mmol) and NaN_3 (1.6 mmol) and ethanol as a solvent. This reaction mixture is stirred at 80 ºC for 20 h. After the completion of the reaction (monitored by TLC), the

catalyst was separated using an external magnet. Further, the crude compound was extracted using ethyl acetate (EtOAc) and brine solution (10 x 3). Then the organic layer was collected, and evaporated using a rota evaporator to obtain the crude compound 1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3a)**. The crude compound was purified by column chromatography (eluent: 3-10% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield (by an average of two runs). A similar procedure was followed in the absence of base and stirred for 2 h to obtain *N*-(p-tolyl)-2-(1*H*-1,2,3-triazol-4-yl)benzamide **(6a)**. The crude compound was purified by column chromatography (eluent: 10-20% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield (by an average of two runs).



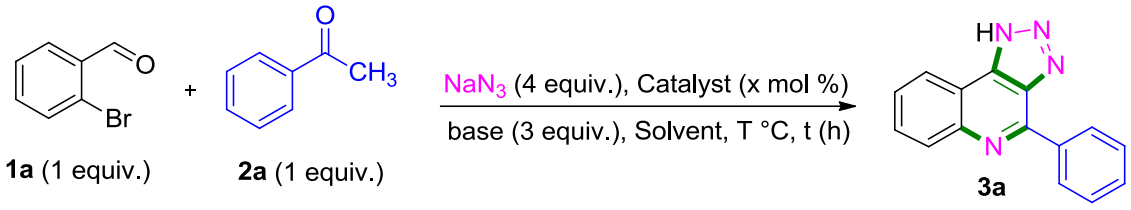
5. Representative procedure for the gram-scale synthesis of 1*H*-[1,2,3]triazolo[4,5-c]quinoline (3a) and *N*-(p-tolyl)-2-(1*H*-1,2,3-triazol-4-yl)benzamide (6a)



In an oven tried 60 mL sealed tube containing 10 mol % of Cu@PANI@Fe_3O_4 (Cu content, w/w: 29%) nanocomposite, Cs_2CO_3 (1.2 mmol) as a base was added 2-bromo benzaldehyde **1a** (0.5 mmol), acetophenone **2a** (0.6 mmol) and NaN_3 (1.6 mmol) and ethanol as a solvent. This reaction mixture is stirred at 80 ºC for 20 h. After the completion of the reaction (monitored by TLC), the catalyst was separated by an external magnet. Further, the crude compound was extracted using ethyl acetate (EtOAc) and brine solution (10 x 3). Then the organic layer was collected, and evaporated using a rota evaporator to obtain the crude compound 1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3a)**. The crude compound was purified by column chromatography (eluent: 3-10% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield

(by an average of two runs). A similar procedure was followed in the absence of base and stirred for 2 h to obtain *N*-(p-tolyl)-2-(1*H*-1,2,3-triazol-4-yl)benzamide **(6a)**. The crude compound was purified by column chromatography (eluent: 10-20% EA/Hexane). The reaction was repeated twice and the product was isolated to determine the yield (by an average of two runs).

6. Table S1: Optimization for the synthesis of 1*H*−[1,2,3]triazolo[4,5-c]quinoline[a]

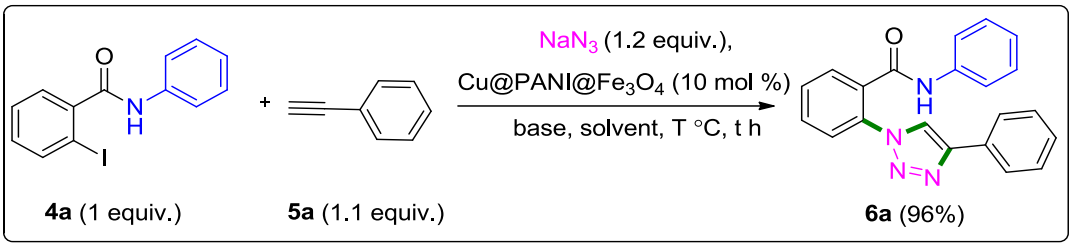


1a (1 equiv.) **2a** (1 equiv.) **3a**

Entry	Nanocomposite (x mol %)	Base	Solvent	Temp./Time T °C / t (h)	Yield[b] %
01	Cu@PANI@Fe_3O_4	Cs_2CO_3	DMSO	100/24	80
02	Cu@PANI@Fe_3O_4	*t*BuOK	DMSO	100/24	trace
03	Cu@PANI@Fe_3O_4	$NaHCO_3$	DMSO	100/24	trace
04	Cu@PANI@Fe_3O_4	K_3PO_4	DMSO	100/24	60
05[c]	Cu@PANI@Fe_3O_4	-	DMSO	100/24	NR
06	**Cu@PANI@Fe_3O_4 (10 mol %)**	**Cs_2CO_3**	**Ethanol**	**80/12**	**95**
07	Cu@PANI@Fe_3O_4	Cs_2CO_3	DMF	100/24	71
08	Cu@PANI@Fe_3O_4	Cs_2CO_3	ACN	100/24	74
09	Cu@PANI@Fe_3O_4	Cs_2CO_3	PEG	100/24	NR
10	Cu@PANI@Fe_3O_4	Cs_2CO_3	Toluene	100/24	NR
11	Cu@PANI@Fe_3O_4 (5 mol %)	Cs_2CO_3	Ethanol	80/12	80
12	Cu@PANI@Fe_3O_4 (3 mol %)	Cs_2CO_3	Ethanol	80/12	66
13[d]	-	Cs_2CO_3	Ethanol	80/12	NR
14	Cu@PANI@Fe_3O_4	Cs_2CO_3	Ethanol	120/12	85
15	Cu@PANI@Fe_3O_4	Cs_2CO_3	Ethanol	100/08	95
16	CuI	Cs_2CO_3	Ethanol	80/12	61
17[e]	PANI@Fe_3O_4	Cs_2CO_3	Ethanol	80/12	NR

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), NaN_3 (1.6 mmol), catalyst (0-25 mol%, 29.61 w/w %), base (1.2 mmol), solvent (2 mL), temperature (80-120 °C) in oil bath for 16 h - 24 h, [c]no base, [d]no catalyst, [e]PANI@Fe_3O_4. [b]Yields are stated upon purification from the silica column (average of two runs).

7. Table S2: Optimization for the synthesis of *N*-(p-tolyl)-2-(1*H*-1,2,3-triazol-4-yl)benzamide



Entry	Catalyst mol %	Base	Solvent	Temp./Time T °C / t (h)	Yield[b] %
01	Cu@PANI@Fe_3O_4	DIPEA	THF	100/12	80
02	Cu@PANI@Fe_3O_4	Cs_2CO_3	THF	100/12	30
03	Cu@PANI@Fe_3O_4	TEA	THF	100/12	60
04	Cu@PANI@Fe_3O_4	$NaHCO_3$	THF	100/12	75
05[c]	Cu@PANI@Fe_3O_4	-	THF	100/12	90
06[d]	-	DIPEA	THF	100/12	NR
07	Cu@PANI@Fe_3O_4	-	Ethylene glycol	100/12	80
08[e]	**Cu@PANI@Fe_3O_4**	**-**	**Ethanol**	**80/2**	**96**
09	Cu@PANI@Fe_3O_4	-	ACN	80/2	20
10	Cu@PANI@Fe_3O_4	-	H_2O	80/2	trace
11	Cu@PANI@Fe_3O_4	-	Ethanol	60/2	40
12	Cu@PANI@Fe_3O_4	-	Ethanol	rt/2	trace
13	Cu@PANI@Fe_3O_4	-	Ethanol	80/6	97

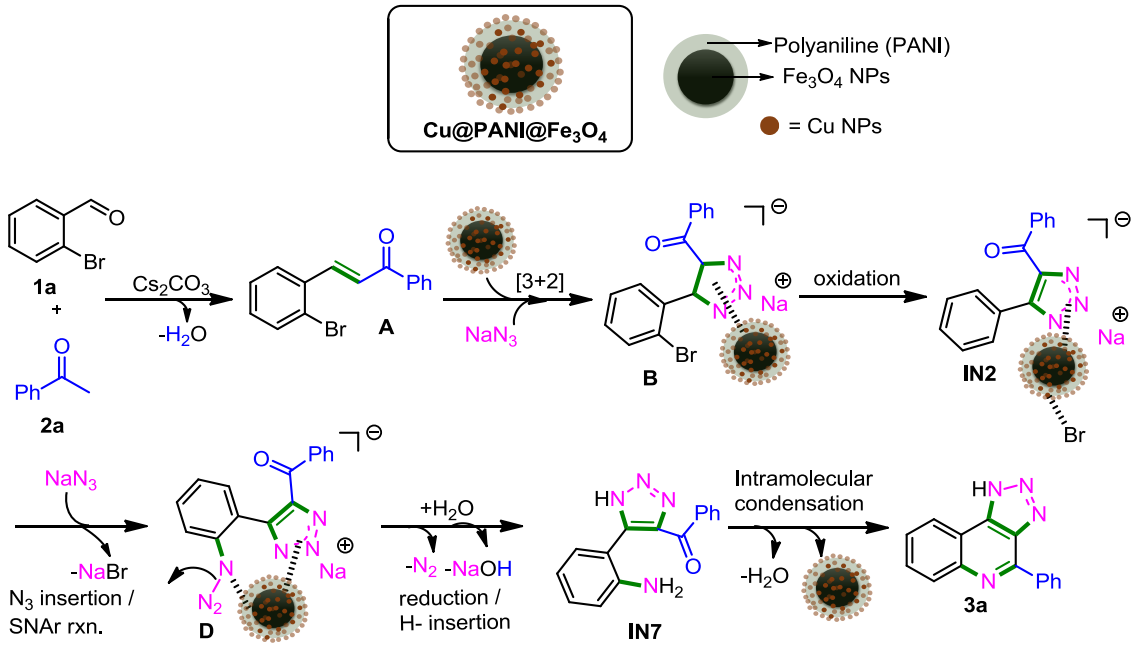
[a]Reaction conditions: 1 (0.4 mmol), 2 (0.4 mmol), NaN_3 (0.6 mmol), Cu@PANI@Fe_3O_4 (0-25 mol%, 29.61% w/w), Solvent (2 mL), temperature (rt - 100 °C) in oil bath for 2 - 12 h, [c]no base, [d]no catalyst, [e]catalyst (10 mol%), [b]Yields are stated upon purification from silica column (average of two runs).

In a similar context, we have attempted to access 2-(1,2,3-triazolyl)benzamide derivatives using the same Cu@PANI@Fe_3O_4 nanocomposite (Table S2). Initially, we examined the reaction by

treating 2-iodo-*N*-phenylbenzamide (**4a**) and phenylacetylene (**5a**) in the presence of NaN_3, DIPEA as a base, and ethanol as solvent at 100 ºC for 12 h resulted in **6a** in 80% yield (entry 1). Next, we tried the reaction using different bases like triethyl amine (TEA), Cs_2CO_3, $NaHCO_3$ and a reaction without base (entry 2-5). Unfortunately, we found that there was not much change by changing the base TEA and $NaHCO_3$ but only a trace amount of product was observed in the case of Cs_2CO_3 while surprisingly the reaction went smoothly in the absence of base and the expected product **6a** was formed in 90% yield (entry 5). Later on, other solvents such as ethanol, ethylene glycol, ACN and H_2O were also included in the optimization process and we found that the reaction was clean when ethanol was used as a solvent (entry 8) while only trace amount of product was formed in ACN and no reaction was seen in H_2O (entry 7 - 10). Further, we tried the reaction even at lower temperatures like room temperature, 60 ºC, and 80 ºC but there was no conversion at rt and 60 ºC while similar conversion as 100 ºC was observed in case of 80 ºC and the reaction was completed in 2 h (entry 11-13).

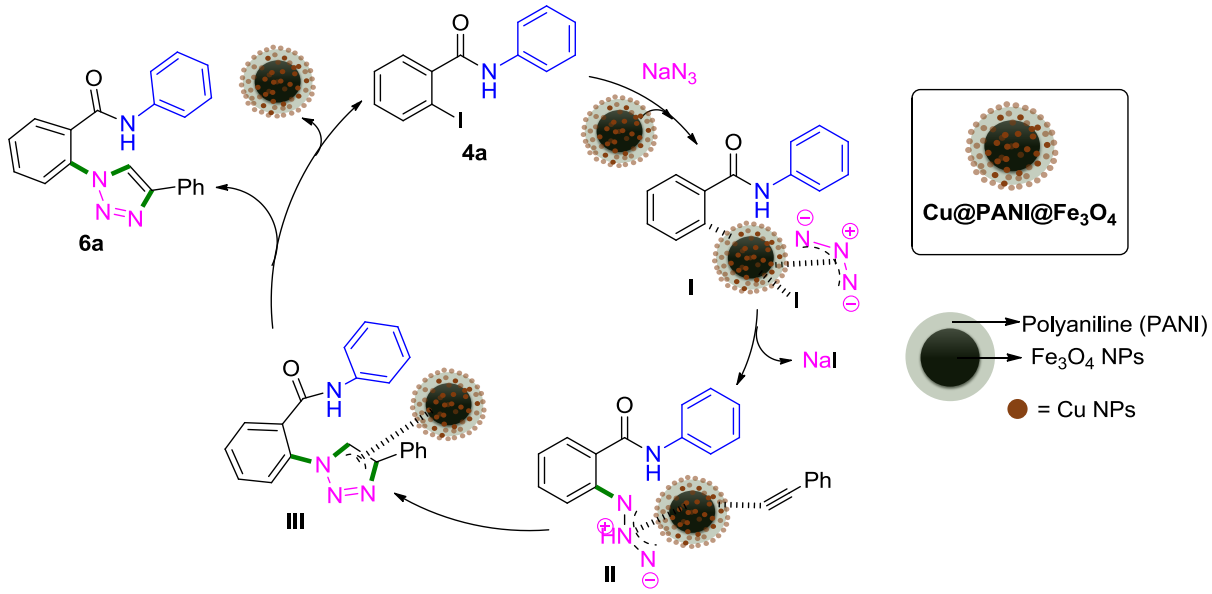
8. Plausible mechanism

Based on control experiments and literature precedents, a plausible mechanism for Cu@PANI@Fe_3O_4 catalyzed reaction sequence has been proposed (Scheme S1). Initially, base-promoted condensation between 2-bromobenzaldehyde (**1a**) and acetophenone (**2a**) forms a 2-bromo chalcone A. Next, [3+2] cycloaddition reaction of activated chalcone with NaN_3 forms a triazoline intermediate B which subsequently undergoes air oxidation to form triazole metal complex IN2. It then subsequently undergoes Cu-catalyzed SNAr reaction which upon N_2 extrusion leads to the form of an amine intermediate IN7. Finally, intermolecular cyclization furnishes desired product **3a** with the recovery of the active catalyst.



Scheme S1. Plausible mechanism for the synthesis of **3a**

Following a similar mechanistic pathway, triazolyl benzamide formation also took place *via* simple copper-catalyzed insertion of azide group followed by simultaneous (3+2) cycloaddition of phenylacetylene and azide group to give the desired triazoles product **6a** (Scheme S2).



Scheme S2. Plausible mechanism for the synthesis of **6a**

9. Catalyst recyclability for 1*H*-[1,2,3]triazolo[4,5-c]quinoline synthesis

The recyclability test for the freshly synthesized Cu@PANI@Fe_3O_4 nanocomposite was examined for 1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3a)** under optimal condition (Figure S6). Once the reaction is completed, the heterogeneous Cu@PANI@Fe_3O_4 nanocomposite was separated from the reaction mixture using external magnet and the crude compound was subjected to column chromatography to obtain the desired product. Later on, the separated catalyst was washed with distilled water (3x10 mL) and ethanol (3x10 mL) and dried at 80 ºC for 12 h. This catalyst is further used for the next cycle and so on. The reaction was repeated up to 5 consecutive cycles and observed that there was no much loss in the yield which tells us the efficiency of the catalyst. The recycled catalyst was subjected to FESEM analysis which demonstrates that copper is stable even after 5 cycles.

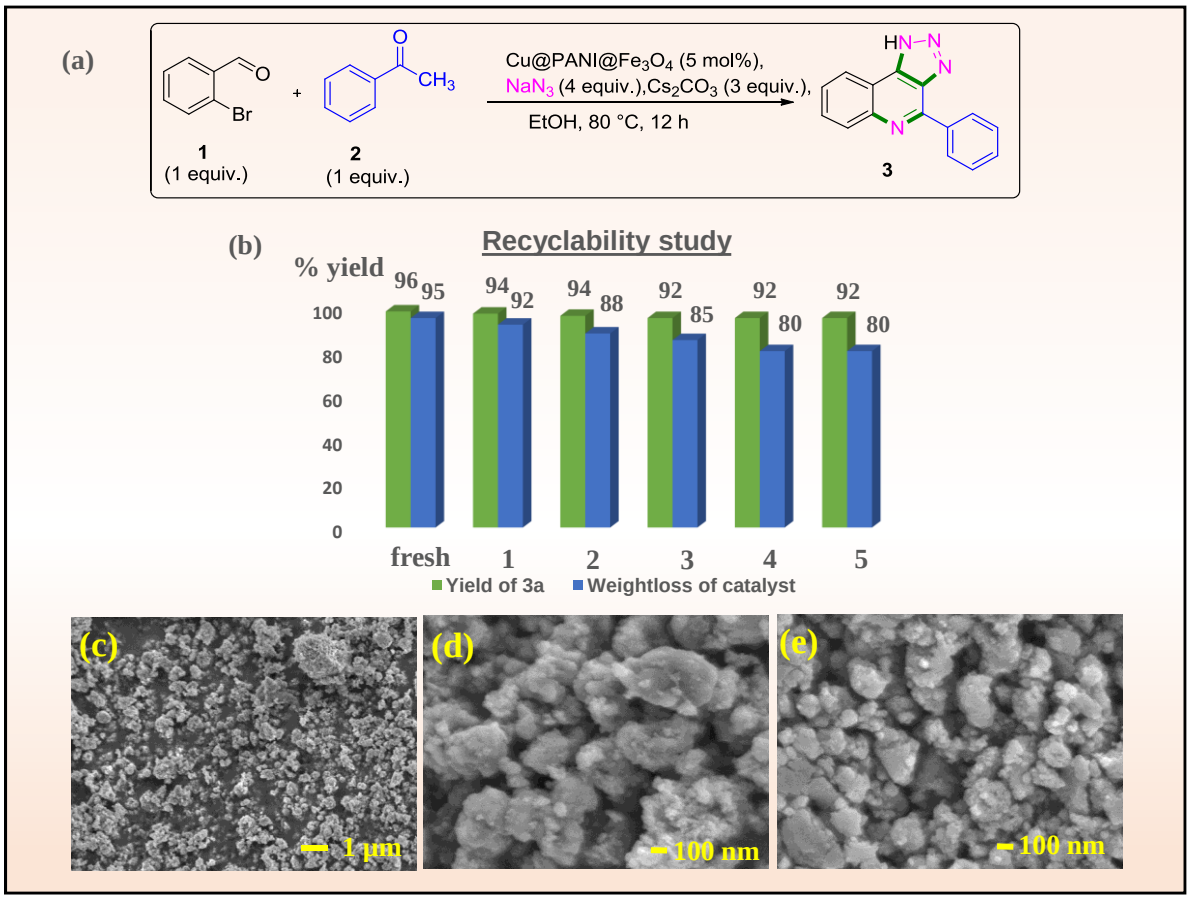


Figure S6. (a) Reaction scheme, (b) Recyclability efficiency of Cu@PAN@Fe_3O_4 nanocomposite, and (d-e) FESEM images of nanocomposite after 5th cycle

10. Biological activity- Anti-cancer study

IC_{50} (μM)	
Compounds	**HCT116**
3a	>50
3c	>50
3d	>50
3e	45.6±0.21
3f	>50
3g	>50
3i	**28.6±0.56**

Table S3. Comparative results of synthesized compounds against colon cancer cells

Materials and Methods:

Cell lines and culture condition:

Human colon cancer cells, HCT116; and Human normal kidney cell lines, HEK; were procured from National centre for Cell Sciences (NCCS) Pune, the cell lines were authenticated by STR analysis and the cells were tested for mycoplasma contaminations. Cells were cultured in IMDM, with 2 mM L- glutamine and 1mM Sodium pyruvate (Thermo Fisher Scientific, Inc.; Waltham, MA USA) containing 10% FBS (Gibco; Grand Island, NY, USA). Cells were cultured in a humidified Incubator with 5% CO_2 at 37 °C.

MTT and Trypan Blue Dye Exclusion assay:

MTT and Trypan Blue dye exclusion assays were performed as described in. Briefly, cells treated with different concentrations of compound **3i** (1, 10, 25, and 50 μM), incubated and subjected to MTT and Trypan Blue dye assays; DMSO was used as a negative control. The plates were subjected to spectrophotometric absorbance at 570 nm using a Tecan Microplate Reader (Tecan Instruments, Switzerland). The Trypan Blue-treated cells were counted using the Thermo Fisher Countess III FL for calculating the percentage of live and dead cells. The data were analysed Microsoft Excel.

Apoptotic analysis by Acridine orange / PI Staining:

The Acridine orange / PI double staining assay was performed following the protocol described in. Briefly, HCT116 cells were seeded at a density of 1 x 105 cells per well in 6-well plates and allowed to attach overnight. Subsequently, they were treated with increasing concentrations of Gin A and incubated for 48 hours before undergoing Hoechst/PI double staining.

Hoechst / Propidium iodide analysis:

The Hoechst/PI double staining assay was conducted following the protocol described in33. Briefly, Rh28 and Rh41 cells were seeded at a density of 1 x 105 cells per well in 6-well plates and allowed to attach overnight. Subsequently, they were treated with increasing concentrations of Gin A and incubated for 48 hours before undergoing Hoechst/PI double staining.

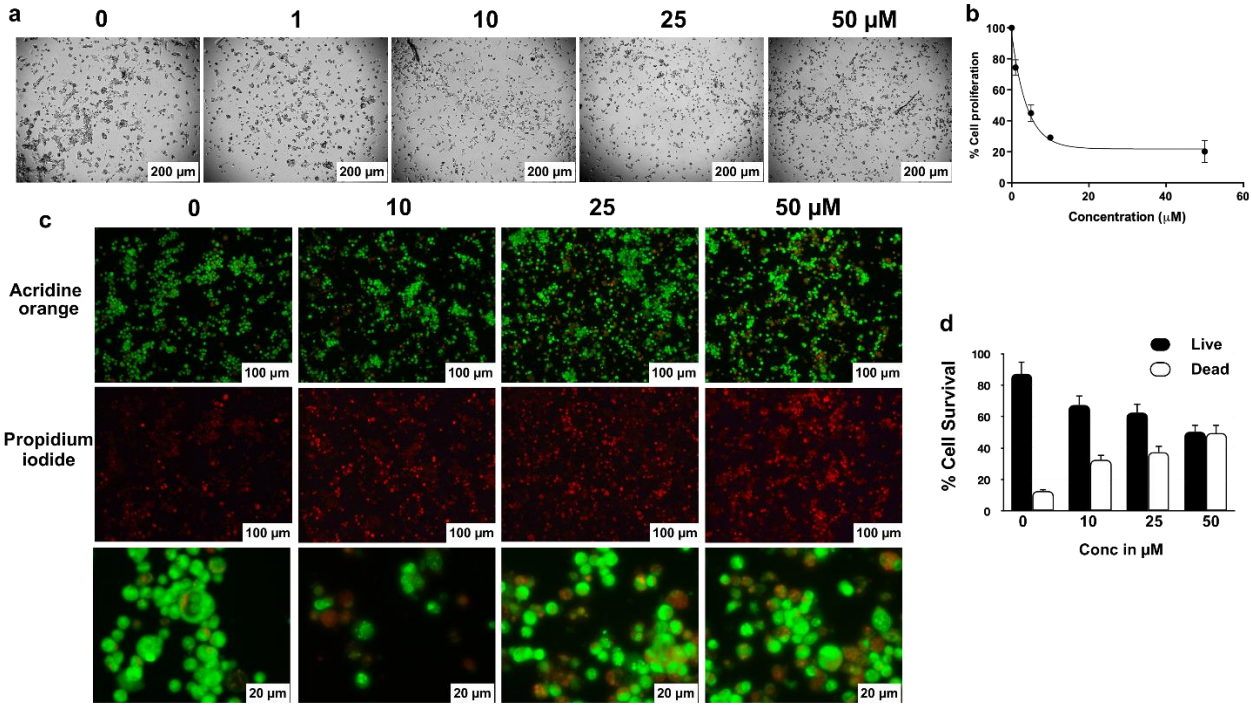


Figure S7: Representation of the effect of compound 3i on proliferation and cell viability

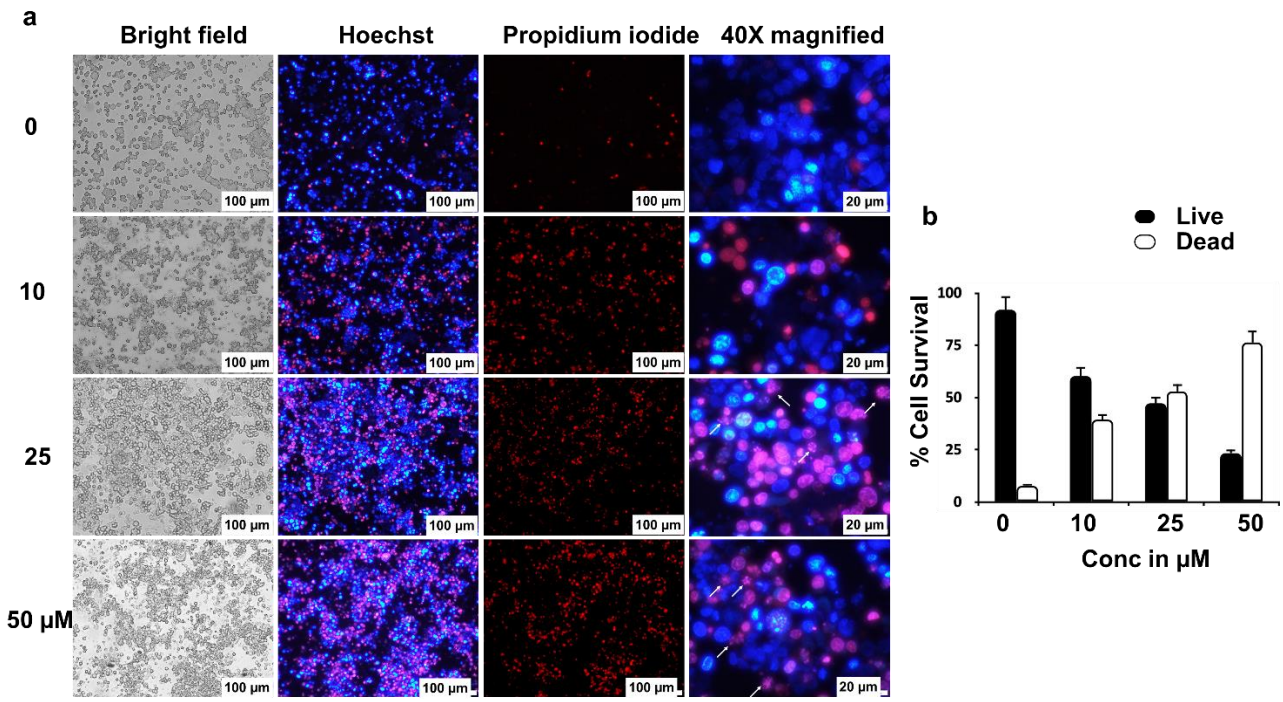


Figure S8: Representation of the effect of compound **3i** on cell death

11. Hot filtration test

A hot filtration test was performed during the triazolo quinoline synthesis process under optimal reaction conditions for 8 hours, at the conclusion of which the reaction mixture was filtered to remove the catalyst in order to determine the leaching of Cu@PAN@Fe_3O_4 nanocomposite. The filtrate was additionally agitated for up to 20 hours, during which the presence of 2-bromo chalcone caused a little rise in the yield of the desired product and the remaining starting material was as such terminating the reaction. By this, catalyst's heterogeneous nature during the triazolo quinoline synthesis was confirmed.

12. Table S4: Comparison with the previous reports

Entry	Catalyst	Ligand	Solvent	Base	Temp./time	Yield	Reference
01	CuO		DMF		100 °C/24 h	80%	EJOC, 2013
02	$Pd(OAc)_2$		DMF	TBAI	120 °C/24 h	84%	RSC Adv.,2013
03	Pd-C/H_2		MeOH		RT/12 h	93%	Tet, 2013
04	$CuBr_2$	L-proline	DMSO	Cs_2CO_3	100 °C/20 h	85%	JOC, 2018

05			DMF	TBAF	RT/8 h	93%	EJOC, 2020
06	**Cu@PANI@Fe_3O_4**	**-**	**EtOH**	**Cs_2CO_3**	**80 °C/12 h**	**95%**	**Present work**

13. Computational studies

All calculation were performed employing a DFT method implemented in the Gaussian 09 suite of programs.[8] For geometry optimization and frequency analysis, we adopted the BP86 functional.[9] During geometry optimization we used the split-valence plus single polarization basis set def2-SVP[10] for non-metals and the Stuttgart/Dresden small core RECP (relativistic effective core potential) plus valence double-ζ-basis set (SDD)[11] for Copper. The geometries were optimized without any symmetry constraints. For each transition state, in addition to analyzing the character of the normal mode associated with the imaginary frequency, intrinsic reaction coordinate (IRC) analysis[12] was performed to confirm that it connects the correct reactant and product on the potential energy surface. To refine the computed energy, singlepoint calculations were performed using the hybrid-meta-GGA M06 functional[13] with the def2- TZVP[10] basis set for nonmetals and SDD for Cu. Solvation energies were evaluated implicitly by a self-consistent reaction field (SCRF) approach for all the intermediates and transitions states, in Ethanol-water solvent (ε = 24.852), using the SMD continuum solvation model.[14] The free energies (ΔG), calculated at the M06(SMD)/SDD/def2- TZVP//BP86/SDD/def2-SVP level are reported throughout the article unless otherwise mentioned. The ΔG value is obtained by augmenting the in solvent electronic energy (ΔE), calculated at M06(SMD)/SDD/def2-TZVP, with the corresponding free energy corrections calculated at BP86/SDD/def2-SVP in the gas phase.

Table S5. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at BP86/SDD(Cu)/Def2-SVP level of theory. E_e^S represents the absolute electronic energy in Hartree at M06/SDD(Cu)/Def2-TZVP level of theory in the ethanol solvent.

A

E_e^S = -3227.250789

C	-3.521977000	-5.994373000	-5.514137000
C	-3.269262000	-5.770118000	-4.139627000
C	-4.542518000	-5.302415000	-6.177949000
H	-2.887411000	-6.729023000	-6.033293000
C	-4.068725000	-4.831113000	-3.446970000
C	-2.147912000	-6.561506000	-3.509008000
C	-5.332061000	-4.369685000	-5.477624000
H	-4.727498000	-5.487770000	-7.248120000
C	-5.092559000	-4.136240000	-4.112371000
H	-3.901470000	-4.629767000	-2.378523000
H	-6.135612000	-3.823807000	-5.997552000
H	-5.707394000	-3.407482000	-3.560665000
O	-1.494743000	-7.357355000	-4.192660000
C	-1.847482000	-6.366269000	-2.061127000
H	-2.451502000	-5.651903000	-1.481926000
C	-0.837033000	-7.070684000	-1.480117000
H	-0.293152000	-7.760601000	-2.148670000
C	-0.395133000	-7.017771000	-0.086151000
C	-1.020750000	-6.168427000	0.868613000
C	0.686985000	-7.815735000	0.389386000
C	-0.606563000	-6.110645000	2.201937000
H	-1.860205000	-5.537131000	0.539193000
C	1.112036000	-7.765738000	1.728439000
C	0.465727000	-6.913181000	2.636035000
H	-1.119185000	-5.438951000	2.907758000
H	1.951013000	-8.398032000	2.053874000
H	0.803057000	-6.878214000	3.683848000
Br	1.629768000	-9.008166000	-0.774132000

NaN_3

E_e^S = -326.5182406

Na	2.144483000	1.416816000	-0.789668000
N	2.080629000	0.479224000	-2.626953000
N	2.043269000	-0.069080000	-3.702916000
N	2.007125000	-0.600202000	-4.745551000

TS1

E_e^S = -5235.745884

C	-1.978241000	0.087545000	-1.176852000
C	-2.613246000	1.347567000	-1.360840000
C	-1.383586000	-0.154129000	0.095678000
C	-2.653809000	2.309553000	-0.347703000
C	-1.440410000	0.801392000	1.113432000
C	-2.075595000	2.059954000	0.928014000
H	-3.052538000	1.573298000	-2.348655000
H	-0.912383000	-1.128495000	0.295757000
H	-3.129604000	3.283655000	-0.540186000
H	-1.000310000	0.579384000	2.099997000
N	-2.036665000	-0.874966000	-2.198418000
C	-1.000785000	-1.762210000	-2.457676000
C	0.357405000	-1.532532000	-2.077917000
C	-1.264609000	-2.956581000	-3.193330000
C	1.366919000	-2.445154000	-2.405068000
C	-0.255949000	-3.869300000	-3.510331000
C	1.076461000	-3.627043000	-3.116513000
H	0.621770000	-0.607242000	-1.546028000
H	-2.303342000	-3.162479000	-3.504222000
H	2.407825000	-2.223704000	-2.114200000
H	-0.497467000	-4.797532000	-4.054376000
N	-2.079697000	3.002284000	1.969107000
C	-3.168753000	3.845831000	2.203032000
C	-2.992998000	5.131618000	2.787616000
C	-4.510704000	3.424732000	1.959078000
C	-4.085425000	5.940040000	3.129491000
C	-5.595848000	4.246188000	2.293553000
C	-5.402298000	5.510616000	2.882027000
H	-1.959239000	5.488329000	2.957396000
H	-4.687124000	2.428252000	1.526775000
H	-3.901605000	6.928833000	3.580999000
H	-6.618667000	3.882441000	2.098434000
H	-6.260883000	6.150506000	3.138035000
Cu	-3.635417000	-0.958504000	-3.16260800
Cu	-0.425877000	3.549382000	2.62691200
N	2.122774000	-4.588781000	-3.420897000
C	2.799328000	-4.508906000	-4.700041000
C	4.086872000	-5.078841000	-4.817163000
C	2.193230000	-3.919612000	-5.826941000
C	4.759037000	-5.053587000	-6.047898000
C	2.875056000	-3.904355000	-7.055970000
C	4.156885000	-4.467824000	-7.176655000
H	4.558055000	-5.548763000	-3.937806000
H	1.196045000	-3.464904000	-5.738256000
H	5.764241000	-5.497968000	-6.123373000
H	2.393380000	-3.436590000	-7.929483000
H	4.684988000	-4.449993000	-8.142572000
H	2.833982000	-4.566632000	-2.675048000
C	-3.559725000	0.809714000	-6.462056000
C	-4.524352000	0.560396000	-5.456123000
C	-3.281784000	2.120288000	-6.871331000
C	-5.223054000	1.652873000	-4.886917000
C	-3.972879000	3.201950000	-6.292328000
C	-4.947450000	2.963867000	-5.306107000
H	-2.521569000	2.303635000	-7.647283000

H	-6.011973000	1.478850000	-4.140958000
H	-3.754873000	4.232899000	-6.613804000
H	-5.502554000	3.806145000	-4.863794000
H	-3.038691000	-0.053300000	-6.903585000
C	-4.763544000	-0.871957000	-5.061512000
O	-4.328355000	-1.812902000	-5.75889600
C	-5.637105000	-1.166126000	-3.859242000
H	-5.746778000	-0.405835000	-3.056980000
C	-5.859558000	-2.621349000	-3.544626000
H	-5.082267000	-3.214049000	-4.073001000
C	-5.940036000	-3.031552000	-2.084592000
C	-6.423168000	-2.153257000	-1.083820000
C	-5.622378000	-4.338087000	-1.648280000
C	-6.536426000	-2.540020000	0.258783000
C	-5.720419000	-4.754456000	-0.311652000
C	-6.177000000	-3.840623000	0.651435000
H	-6.718185000	-1.132908000	-1.373252000
Br	-5.001897000	-5.686263000	-2.916613000
H	-6.903985000	-1.817978000	1.003989000
H	-5.437702000	-5.778734000	-0.027863000
H	-6.250628000	-4.151856000	1.704870000
Na	-7.471356000	-5.207701000	-4.47632100
N	-7.213200000	-3.032534000	-4.212438000
N	-7.766077000	-1.951965000	-4.646652000
N	-7.324524000	-0.811574000	-4.631692000
Cu	1.477856000	-6.574296000	-3.104785000

IN2

E_e^S = -5234.640273

C	-1.746332000	-0.685451000	-0.626882000
C	-2.781063000	-0.257397000	0.257241000
C	-0.426784000	-0.757254000	-0.081991000
C	-2.524168000	0.096417000	1.580155000
C	-0.174461000	-0.421938000	1.247538000
C	-1.208091000	0.016545000	2.123257000
H	-3.808286000	-0.180840000	-0.141366000
H	0.398325000	-1.129408000	-0.707351000
H	-3.348122000	0.450793000	2.218156000
H	0.847401000	-0.515541000	1.651911000
N	-2.071495000	-1.067310000	-1.926145000
C	-1.158096000	-1.015859000	-2.977785000
C	-0.106531000	-0.057300000	-3.079473000
C	-1.312258000	-1.909388000	-4.080629000
C	0.726095000	0.007743000	-4.205530000
C	-0.481182000	-1.848811000	-5.200126000
C	0.555323000	-0.890248000	-5.277263000
H	0.039188000	0.672016000	-2.269504000
H	-2.111182000	-2.668308000	-4.035718000
H	1.516250000	0.771918000	-4.241450000
H	-0.635716000	-2.562132000	-6.027413000
N	-0.902329000	0.367214000	3.441740000
C	-1.816148000	0.181491000	4.488092000
C	-1.879600000	1.084900000	5.583880000
C	-2.649883000	-0.974116000	4.544440000
C	-2.711576000	0.841339000	6.686117000
C	-3.486974000	-1.201838000	5.644578000
C	-3.529372000	-0.302006000	6.727045000
H	-1.262587000	2.002301000	5.540946000
H	-2.607791000	-1.705252000	3.723063000
H	-2.731693000	1.566500000	7.515925000
H	-4.110811000	-2.110746000	5.660136000
H	-4.191615000	-0.488141000	7.586617000
Cu	-3.811048000	-1.581105000	-2.34508800
Cu	0.419574000	1.647134000	3.72419800
N	1.347032000	-0.839944000	-6.496255000
C	2.618540000	-0.146589000	-6.494087000
C	3.821042000	-0.880011000	-6.477481000
C	2.655151000	1.262252000	-6.550193000
C	5.054167000	-0.207468000	-6.519542000
C	3.891509000	1.927830000	-6.574653000
C	5.093336000	1.196949000	-6.561509000
H	3.791435000	-1.980984000	-6.429469000
H	1.710109000	1.827162000	-6.589794000
H	5.989787000	-0.788311000	-6.512385000
H	3.913551000	3.027934000	-6.619696000
H	6.060461000	1.722385000	-6.590340000
H	1.491920000	-1.805191000	-6.825882000
C	-7.440296000	-4.240015000	-2.988923000
C	-7.010403000	-3.504507000	-4.123880000
C	-8.477960000	-5.172295000	-3.100752000
C	-7.643135000	-3.727905000	-5.373229000
C	-9.099935000	-5.389009000	-4.346473000
C	-8.678408000	-4.667822000	-5.478518000
H	-8.806215000	-5.737804000	-2.214356000
H	-7.301519000	-3.172139000	-6.257338000
H	-9.916331000	-6.123913000	-4.433760000
H	-9.162949000	-4.837983000	-6.452832000
H	-6.941972000	-4.059464000	-2.025073000
C	-5.920850000	-2.516757000	-3.964010000
O	-5.474462000	-2.302033000	-2.78693700
C	-5.339490000	-1.807030000	-5.104727000
C	-4.852140000	-0.467090000	-5.178659000
C	-4.920821000	0.683253000	-4.251296000
C	-3.736745000	1.427933000	-4.008846000
C	-6.107291000	1.140521000	-3.619783000
C	-3.724490000	2.549210000	-3.169550000
C	-6.103258000	2.259156000	-2.767399000
C	-4.910269000	2.962445000	-2.538566000
H	-2.808381000	1.086654000	-4.490652000
Br	-7.799427000	0.302992000	-3.944214000
H	-2.783467000	3.094439000	-2.999014000

H	-7.043661000	2.582278000	-2.297209000
H	-4.915068000	3.836696000	-1.868748000
Na	-2.698633000	-0.357210000	-8.11116600
N	-4.262846000	-0.349756000	-6.390672000
N	-4.370041000	-1.554828000	-7.019064000
N	-5.024809000	-2.432539000	-6.284013000
Cu	0.172495000	-0.136085000	-8.119631000

TS2

E_e^S = -5234.593845

C	-2.436184000	0.792822000	-0.296867000
C	-3.257295000	-0.325283000	-0.670506000
C	-3.096004000	1.881797000	0.375138000
C	-4.614291000	-0.369208000	-0.393396000
C	-4.450371000	1.830465000	0.661355000
C	-5.260964000	0.704398000	0.304324000
H	-2.777569000	-1.153391000	-1.221365000
H	-2.501765000	2.742040000	0.716282000
H	-5.211278000	-1.230608000	-0.727436000
H	-4.927841000	2.658366000	1.213821000
N	-1.092075000	0.739057000	-0.543398000
C	-0.304466000	1.892210000	-0.516742000
C	-0.691688000	3.089393000	-1.183597000
C	0.962621000	1.863936000	0.126113000
C	0.154539000	4.200440000	-1.208157000
C	1.796038000	2.986431000	0.123968000
C	1.405225000	4.158221000	-0.553498000
H	-1.646352000	3.118987000	-1.730273000
H	1.265443000	0.955817000	0.672695000
H	-0.152445000	5.108239000	-1.754834000
H	2.763381000	2.936332000	0.643874000
N	-6.605008000	0.707048000	0.615682000
C	-7.366807000	-0.471571000	0.721727000
C	-8.705116000	-0.512042000	0.250653000
C	-6.858556000	-1.621765000	1.388013000
C	-9.505186000	-1.648667000	0.437809000
C	-7.663077000	-2.756079000	1.561611000
C	-8.989513000	-2.782765000	1.090023000
H	-9.101852000	0.371096000	-0.282935000
H	-5.835706000	-1.601929000	1.793285000
H	-10.539836000	-1.649764000	0.05914300
H	-7.248311000	-3.629872000	2.089608000
H	-9.615072000	-3.677258000	1.233288000
Cu	-0.282689000	-1.055680000	-0.77468500
Cu	-7.588838000	2.289166000	0.47862800
N	2.223987000	5.361415000	-0.560177000
C	3.674273000	5.196551000	-0.499964000
C	4.324822000	5.116354000	0.745368000
C	4.417110000	5.131788000	-1.693480000
C	5.721011000	4.964412000	0.792780000
C	5.814265000	4.994767000	-1.638383000
C	6.467955000	4.906457000	-0.396787000
H	3.731936000	5.183518000	1.672344000
H	3.902198000	5.181537000	-2.666720000
H	6.226524000	4.900599000	1.768813000
H	6.392542000	4.949557000	-2.574368000
H	7.562545000	4.794523000	-0.356223000
H	1.994629000	5.886206000	-1.418099000
Cu	1.600547000	6.736562000	0.82237700
C	6.420783000	-3.558861000	0.844436000
C	5.186257000	-3.388125000	1.516946000
C	7.613725000	-3.670180000	1.569362000
C	5.168356000	-3.324358000	2.931323000
C	3.942342000	-3.298832000	0.696798000
C	7.588783000	-3.605388000	2.976630000
H	8.570307000	-3.807036000	1.040194000
C	6.367803000	-3.429531000	3.652597000
H	4.212554000	-3.163069000	3.450479000
H	8.527166000	-3.691707000	3.548090000
H	6.349794000	-3.374165000	4.752583000
O	4.006901000	-3.379777000	-0.557347000
C	2.626040000	-3.073886000	1.319505000
C	1.354616000	-3.417862000	0.796515000
C	0.652830000	-4.164725000	-0.258812000
C	0.757785000	-5.558354000	-0.488762000
C	-0.162883000	-3.349645000	-1.100429000
C	0.046122000	-6.141747000	-1.551515000
H	1.386517000	-6.182208000	0.166256000
C	-0.854027000	-3.951856000	-2.166311000
C	-0.759713000	-5.343051000	-2.386080000
H	0.118584000	-7.226893000	-1.727729000
H	-1.467634000	-3.341135000	-2.850336000
H	-1.313269000	-5.804859000	-3.220619000
N	0.462247000	-2.645647000	1.481094000
N	1.123466000	-1.881014000	2.377443000
N	2.416858000	-2.138725000	2.316735000
H	6.409310000	-3.605098000	-0.255213000
Br	1.372579000	-2.491205000	-2.258897000
Na	5.459923000	-1.565792000	-2.078874000

IN3

E_e^S = -5072.43578

C	-0.384614000	-0.810156000	-2.847803000
C	-1.354254000	-0.794589000	-1.796869000
C	0.910137000	-1.336056000	-2.534981000
C	-1.045323000	-1.237864000	-0.512943000
C	1.211656000	-1.782804000	-1.253572000
C	0.249109000	-1.753095000	-0.198391000
H	-2.349097000	-0.373601000	-2.016216000
H	1.654665000	-1.428513000	-3.338518000

H	-1.805037000	-1.172968000	0.280869000
H	2.206557000	-2.207629000	-1.036951000
N	-0.754823000	-0.378390000	-4.106746000
C	0.098972000	0.216950000	-5.002716000
C	1.252483000	0.965424000	-4.600676000
C	-0.206292000	0.210773000	-6.399852000
C	2.048082000	1.633969000	-5.535165000
C	0.598223000	0.872906000	-7.327669000
C	1.741314000	1.587291000	-6.910259000
H	1.486455000	1.056671000	-3.530159000
H	-1.093413000	-0.340888000	-6.747289000
H	2.913654000	2.231473000	-5.199628000
H	0.339203000	0.826530000	-8.398860000
N	0.614889000	-2.184728000	1.073642000
C	-0.301499000	-2.732932000	1.975193000
C	-0.151951000	-2.538652000	3.377497000
C	-1.360629000	-3.587010000	1.544498000
C	-1.001668000	-3.167532000	4.298257000
C	-2.210599000	-4.201683000	2.473092000
C	-2.045437000	-4.001857000	3.857938000
H	0.652583000	-1.864421000	3.724684000
H	-1.487749000	-3.781913000	0.468972000
H	-0.852549000	-2.989561000	5.376270000
H	-3.013057000	-4.861693000	2.103825000
H	-2.720043000	-4.487915000	4.580213000
Cu	-2.463991000	-1.191363000	-4.73127900
Cu	2.237147000	-1.549827000	1.78142400
N	2.569781000	2.288493000	-7.880962000
C	3.661235000	1.571761000	-8.506802000
C	4.272197000	0.465332000	-7.884228000
C	4.144080000	2.025800000	-9.754862000
C	5.355173000	-0.174936000	-8.509941000
C	5.223142000	1.375742000	-10.37170100
C	5.837883000	0.271868000	-9.752512000
H	3.888000000	0.102471000	-6.919863000
H	3.670632000	2.897063000	-10.23751500
H	5.820005000	-1.043789000	-8.017022000
H	5.585491000	1.737473000	-11.34747400
H	6.684697000	-0.238439000	-10.23755400
H	1.967214000	2.674448000	-8.623824000
Cu	3.311760000	4.121626000	-7.17478000
C	-0.989008000	-8.587125000	-6.989815000
C	-0.590507000	-7.307047000	-6.533438000
C	-0.043151000	-9.589531000	-7.240924000
C	0.787757000	-7.055775000	-6.333075000
C	-1.711822000	-6.309095000	-6.293687000
C	1.326314000	-9.330966000	-7.038484000
H	-0.372117000	-10.580227000	-7.59584800
C	1.733909000	-8.064499000	-6.585230000
H	1.091993000	-6.058986000	-5.980106000
H	2.073813000	-10.117722000	-7.23411700
H	2.804186000	-7.855233000	-6.423962000
O	-2.878208000	-6.686409000	-6.49802700
C	-1.450526000	-4.930944000	-5.833447000
C	-2.375696000	-3.887881000	-5.556155000
C	-3.805401000	-3.577416000	-5.538963000
C	-4.853621000	-4.471967000	-5.855543000
C	-4.110506000	-2.238510000	-5.147630000
C	-6.187678000	-4.040068000	-5.773809000
H	-4.584448000	-5.494810000	-6.158332000
C	-5.442800000	-1.820267000	-5.070674000
C	-6.483407000	-2.724880000	-5.380878000
H	-7.002093000	-4.741249000	-6.019945000
H	-5.675739000	-0.785115000	-4.777967000
H	-7.531007000	-2.385106000	-5.315268000
N	-1.593118000	-2.836989000	-5.170575000
N	-0.285562000	-3.165944000	-5.200119000
N	-0.189693000	-4.411995000	-5.594247000
H	-2.066466000	-8.759018000	-7.136187000
Br	-3.600211000	0.868730000	-4.571425000

IN4

E_e^S = -2498.201636

C	0.416052000	-1.063362000	-2.322763000
C	-0.493150000	-1.843920000	-1.546315000
C	1.096798000	-0.001414000	-1.649304000
C	-0.708110000	-1.596116000	-0.196042000
C	0.900400000	0.228538000	-0.291533000
C	0.001577000	-0.558303000	0.488807000
H	-1.066093000	-2.637927000	-2.054909000
H	1.833532000	0.605464000	-2.196231000
H	-1.448887000	-2.196231000	0.352438000
H	1.469216000	1.028150000	0.215859000
N	0.657926000	-1.402945000	-3.648154000
C	1.166611000	-0.446215000	-4.551672000
C	0.705668000	0.898028000	-4.597718000
C	2.112275000	-0.859233000	-5.526341000
C	1.169874000	1.778553000	-5.578018000
C	2.582492000	0.022491000	-6.506395000
C	2.110095000	1.349189000	-6.542401000
H	-0.056434000	1.234649000	-3.879144000
H	2.479862000	-1.897612000	-5.498932000
H	0.784889000	2.811821000	-5.608258000
H	3.311883000	-0.330929000	-7.248972000
N	-0.175892000	-0.279765000	1.834228000
C	-0.680743000	-1.208456000	2.763064000
C	-1.550593000	-0.786074000	3.801755000
C	-0.275545000	-2.572084000	2.747128000
C	-1.997458000	-1.681649000	4.784203000
C	-0.738753000	-3.463219000	3.725275000
C	-1.601010000	-3.030500000	4.750288000

H	-1.883134000	0.268480000	3.813773000
H	0.425776000	-2.918145000	1.973074000
H	-2.672403000	-1.322236000	5.577383000
H	-0.404394000	-4.512752000	3.693376000
H	-1.955809000	-3.736413000	5.516817000
Cu	-0.043715000	-2.899072000	-4.503292000
Cu	-0.043822000	1.468160000	2.430767000
N	2.593553000	2.315270000	-7.511469000
C	3.024662000	1.817421000	-8.814708000
C	4.358473000	1.410848000	-9.006975000
C	2.104936000	1.759732000	-9.878662000
C	4.767243000	0.937549000	-10.265535000
C	2.524293000	1.298531000	-11.137825000
C	3.853230000	0.882433000	-11.332194000
H	5.072349000	1.480165000	-8.169500000
H	1.059029000	2.070078000	-9.721699000
H	5.811112000	0.620009000	-10.412998000
H	1.803463000	1.258381000	-11.969171000
H	4.177779000	0.516807000	-12.318656000
H	1.850968000	3.016328000	-7.656474000
Cu	4.025311000	3.560020000	-6.685634000
C	-2.039315000	-9.298431000	-8.580717000
C	-1.090008000	-8.468809000	-7.934340000
C	-1.643807000	-10.480123000	-9.219756000
C	0.271759000	-8.854935000	-7.943956000
C	-1.637935000	-7.219266000	-7.277869000
C	-0.286757000	-10.856734000	-9.224396000
H	-2.395047000	-11.114356000	-9.717806000
C	0.664078000	-10.041836000	-8.586102000
H	1.006942000	-8.209176000	-7.441647000
H	0.027698000	-11.786649000	-9.725977000
H	1.727217000	-10.332310000	-8.586137000
O	-2.859632000	-7.005402000	-7.339623000
C	-0.768259000	-6.250400000	-6.569789000
C	-1.138061000	-5.047822000	-5.912063000
C	-2.300649000	-4.204403000	-5.596145000
C	-3.649672000	-4.445612000	-5.940416000
C	-1.984174000	-3.028224000	-4.861045000
C	-4.642815000	-3.526595000	-5.554150000
H	-3.881738000	-5.359616000	-6.508227000
C	-2.966357000	-2.116369000	-4.475688000
C	-4.314568000	-2.370175000	-4.827884000
H	-5.692675000	-3.721712000	-5.826413000
H	-2.713019000	-1.209402000	-3.900479000
H	-5.100155000	-1.656571000	-4.528328000
N	0.041986000	-4.547739000	-5.434563000
N	1.078026000	-5.350918000	-5.757193000
N	0.601745000	-6.369926000	-6.435160000
H	-3.092584000	-8.979604000	-8.560163000

TS3

E_e^S = -2824.712289

C	2.194401000	0.886492000	0.414247000
C	3.084514000	-0.160535000	0.833083000
C	2.778821000	1.969910000	-0.332397000
C	4.436561000	-0.144580000	0.529978000
C	4.128501000	1.977808000	-0.644116000
C	5.008266000	0.921297000	-0.241182000
H	2.662808000	-0.980883000	1.440157000
H	2.130454000	2.774456000	-0.709017000
H	5.087608000	-0.950538000	0.899514000
H	4.547936000	2.797730000	-1.252734000
N	0.860229000	0.772114000	0.692095000
C	0.007854000	1.876018000	0.616900000
C	0.338273000	3.129519000	1.206340000
C	-1.267012000	1.739903000	0.003906000
C	-0.569288000	4.191143000	1.185908000
C	-2.162845000	2.812355000	-0.039823000
C	-1.827201000	4.041361000	0.561573000
H	1.299456000	3.243943000	1.729933000
H	-1.527469000	0.786199000	-0.483683000
H	-0.304655000	5.144766000	1.673522000
H	-3.135030000	2.678335000	-0.535261000
N	6.344110000	0.980971000	-0.580837000
C	7.169766000	-0.157432000	-0.636102000
C	8.516529000	-0.095801000	-0.192195000
C	6.715867000	-1.370822000	-1.225053000
C	9.376524000	-1.194901000	-0.331623000
C	7.580421000	-2.466587000	-1.351174000
C	8.914555000	-2.391847000	-0.907282000
H	8.871919000	0.837496000	0.281835000
H	5.686368000	-1.431603000	-1.608850000
H	10.416252000	-1.116322000	0.02430000
H	7.206601000	-3.391251000	-1.819768000
H	9.587354000	-3.256805000	-1.012907000
Cu	0.158725000	-1.048625000	1.04206600
Cu	7.238536000	2.620827000	-0.55480800
N	-2.712921000	5.195332000	0.517478000
C	-4.152312000	4.946543000	0.497718000
C	-4.819708000	4.758248000	-0.726874000
C	-4.868491000	4.909554000	1.708585000
C	-6.205604000	4.526101000	-0.735746000
C	-6.256340000	4.691780000	1.691216000
C	-6.926343000	4.495439000	0.470881000
H	-4.248517000	4.804677000	-1.668624000
H	-4.339688000	5.044188000	2.666210000
H	-6.724275000	4.377810000	-1.695562000
H	-6.814038000	4.668571000	2.640402000
H	-8.013333000	4.320405000	0.460132000
H	-2.498313000	5.780857000	1.339150000
Cu	-2.194001000	6.520864000	-0.95386500

C	-6.419514000	-4.011642000	-0.288838000
C	-5.209115000	-3.811432000	-0.996175000
C	-7.617124000	-4.231141000	-0.980625000
C	-5.220523000	-3.828686000	-2.411951000
C	-3.957642000	-3.605534000	-0.209181000
C	-7.621433000	-4.246570000	-2.389513000
H	-8.554605000	-4.390354000	-0.424226000
C	-6.424911000	-4.042210000	-3.100303000
H	-4.285032000	-3.644583000	-2.959726000
H	-8.563582000	-4.418059000	-2.934974000
H	-6.430033000	-4.049646000	-4.201791000
O	-3.994735000	-3.617276000	1.048629000
C	-2.667799000	-3.343842000	-0.871629000
C	-1.369572000	-3.585464000	-0.357256000
C	-0.607360000	-4.229681000	0.723504000
C	-0.628566000	-5.611357000	1.034333000
C	0.175721000	-3.323012000	1.499904000
C	0.134327000	-6.091652000	2.113020000
H	-1.232511000	-6.306186000	0.429345000
C	0.919261000	-3.823029000	2.583220000
C	0.908352000	-5.202273000	2.883522000
H	0.127007000	-7.167138000	2.352018000
H	1.509381000	-3.140457000	3.218231000
H	1.502358000	-5.583406000	3.730896000
N	-0.535202000	-2.805524000	-1.103451000
N	-1.255049000	-2.132133000	-2.027399000
N	-2.530345000	-2.457713000	-1.924546000
H	-6.385489000	-3.993480000	0.811167000
N	-1.273246000	-0.856000000	2.240195000
N	-1.878745000	-1.966983000	2.713906000
N	-1.248703000	-3.040937000	2.275008000
Na	0.868606000	-3.676721000	-2.399730000

IN5

E_e^S = -2715.25079

C	3.850441000	-3.320275000	3.797467000
C	2.952771000	-2.592199000	4.636166000
C	5.037847000	-3.824839000	4.412795000
C	3.212147000	-2.379342000	5.989286000
C	5.286430000	-3.629846000	5.769206000
C	4.386914000	-2.906903000	6.607139000
H	2.055874000	-2.144735000	4.172411000
H	5.743268000	-4.423149000	3.816650000
H	2.514249000	-1.774808000	6.588161000
H	6.192998000	-4.061857000	6.226976000
N	3.504485000	-3.566546000	2.468846000
C	4.478767000	-3.729725000	1.484184000
C	5.732145000	-3.048484000	1.504153000
C	4.204717000	-4.547832000	0.350948000
C	6.646533000	-3.188590000	0.457297000
C	5.121390000	-4.694228000	-0.693943000
C	6.354262000	-4.012042000	-0.652288000
H	5.965871000	-2.367636000	2.335864000
H	3.240293000	-5.080474000	0.312245000
H	7.599794000	-2.634007000	0.493818000
H	4.870291000	-5.340200000	-1.547720000
N	4.691130000	-2.716708000	7.951936000
C	3.706756000	-2.489549000	8.928906000
C	3.933476000	-1.582699000	9.997433000
C	2.488218000	-3.226071000	8.935719000
C	2.996591000	-1.422714000	11.02900800
C	1.551169000	-3.049401000	9.962869000
C	1.792841000	-2.149082000	11.01797900
H	4.865876000	-0.987456000	9.991743000
H	2.301966000	-3.960476000	8.137494000
H	3.205655000	-0.709730000	11.84260600
H	0.620389000	-3.639491000	9.946517000
H	1.052205000	-2.017474000	11.82157000
Cu	1.688154000	-3.700780000	2.04986200
Cu	6.420049000	-2.242424000	8.42650300
N	7.364292000	-4.170977000	-1.685842000
C	6.901229000	-4.395428000	-3.052639000
C	6.671901000	-5.705924000	-3.512070000
C	6.702635000	-3.298495000	-3.912087000
C	6.236074000	-5.915494000	-4.831777000
C	6.280439000	-3.516115000	-5.234450000
C	6.042227000	-4.823128000	-5.695114000
H	6.852758000	-6.556129000	-2.833697000
H	6.875239000	-2.273183000	-3.546225000
H	6.059430000	-6.942136000	-5.188348000
H	6.132687000	-2.656090000	-5.906051000
H	5.709002000	-4.990629000	-6.731046000
H	7.952635000	-3.323709000	-1.678146000
Cu	8.809050000	-5.548992000	-1.18044200
C	-7.150494000	-1.096427000	2.180720000
C	-6.442862000	-2.138589000	2.828798000
C	-8.337658000	-0.587385000	2.722161000
C	-6.959164000	-2.663169000	4.037794000
C	-5.180756000	-2.613404000	2.131929000
C	-8.845032000	-1.116400000	3.924687000
H	-8.874044000	0.225581000	2.206131000
C	-8.152999000	-2.152317000	4.575630000
H	-6.398527000	-3.462483000	4.543905000
H	-9.780388000	-0.720038000	4.352912000
H	-8.545906000	-2.570057000	5.516927000
O	-4.889006000	-2.111597000	1.035363000
C	-4.294782000	-3.645937000	2.726186000
C	-3.060753000	-4.182988000	2.211749000
C	-2.354195000	-3.999113000	0.942454000
C	-3.105744000	-3.959217000	-0.255418000
C	-0.877006000	-3.866261000	0.856451000

C	-2.507809000	-3.808174000	-1.510058000
H	-4.196958000	-4.055553000	-0.189454000
C	-0.320616000	-3.699740000	-0.482046000
C	-1.098645000	-3.667724000	-1.624369000
H	-3.137590000	-3.800974000	-2.413931000
H	-6.732871000	-0.706821000	1.239674000
H	-0.632965000	-3.540409000	-2.615108000
N	-2.580638000	-5.002094000	3.191065000
N	-3.435636000	-4.969333000	4.236461000
N	-4.447057000	-4.154047000	3.984722000
N	-0.092313000	-3.866317000	1.936319000
Na	-0.529058000	-4.811547000	3.99984100
H	0.776370000	-3.597494000	-0.536606000

TS4

E_e^S = -2629.452805

C	-1.894187000	0.593848000	0.510883000
C	-1.425290000	1.826852000	1.067630000
C	-3.070641000	0.666553000	-0.306724000
C	-2.069488000	3.035040000	0.837650000
C	-3.706835000	1.876966000	-0.546837000
C	-3.235200000	3.110656000	0.005978000
H	-0.537086000	1.792969000	1.721761000
H	-3.446494000	-0.245026000	-0.794393000
H	-1.692689000	3.948056000	1.321948000
H	-4.592741000	1.913352000	-1.204935000
N	-1.172619000	-0.563902000	0.729079000
C	-1.758634000	-1.829274000	0.597816000
C	-3.088357000	-2.111279000	1.025207000
C	-0.972288000	-2.909847000	0.103697000
C	-3.613869000	-3.405667000	0.938438000
C	-1.509860000	-4.196234000	0.005792000
C	-2.836828000	-4.456673000	0.408470000
H	-3.691580000	-1.310072000	1.477752000
H	0.066214000	-2.705328000	-0.214601000
H	-4.627951000	-3.620180000	1.315782000
H	-0.888262000	-5.010946000	-0.402308000
N	-3.932106000	4.276815000	-0.237768000
C	-3.348105000	5.546288000	-0.139233000
C	-4.112826000	6.648988000	0.332697000
C	-2.018973000	5.806503000	-0.582710000
C	-3.576973000	7.943908000	0.365594000
C	-1.490247000	7.103730000	-0.538312000
C	-2.258357000	8.184269000	-0.063060000
H	-5.142722000	6.457092000	0.682549000
H	-1.415268000	4.980694000	-0.988381000
H	-4.196781000	8.774821000	0.740816000
H	-0.461058000	7.273604000	-0.894794000
H	-1.835135000	9.200521000	-0.031772000
Cu	0.686347000	-0.491955000	1.07668600
Cu	-5.813616000	4.204056000	-0.45520100
N	-3.374160000	-5.801647000	0.328017000
C	-4.222209000	-6.161629000	-0.791339000
C	-4.954666000	-5.201188000	-1.515836000
C	-4.333502000	-7.528053000	-1.133889000
C	-5.788641000	-5.611008000	-2.570391000
C	-5.165363000	-7.924349000	-2.191119000
C	-5.901086000	-6.968608000	-2.915583000
H	-4.862226000	-4.135420000	-1.263140000
H	-3.766132000	-8.281377000	-0.562486000
H	-6.351812000	-4.849579000	-3.133310000
H	-5.237489000	-8.992887000	-2.449555000
H	-6.554709000	-7.280700000	-3.744901000
H	-2.595460000	-6.476018000	0.372773000
Cu	-4.357859000	-6.387444000	2.09673400
C	9.973284000	0.341875000	0.924868000
C	8.841450000	0.070008000	0.118488000
C	11.253066000	-0.082310000	0.54226900
C	9.027280000	-0.641726000	-1.090581000
C	7.507407000	0.585715000	0.654220000
C	11.428478000	-0.789737000	-0.66256300
H	12.121478000	0.138138000	1.18545200
C	10.312806000	-1.064446000	-1.47259500
H	8.139378000	-0.841601000	-1.710651000
H	12.433806000	-1.125629000	-0.96779400
H	10.441953000	-1.617508000	-2.41792100
O	7.527812000	1.198972000	1.736143000
C	6.240907000	0.363582000	-0.068959000
C	4.879056000	0.593855000	0.351140000
C	4.295010000	1.280102000	1.505267000
C	4.906671000	2.447152000	2.023212000
C	3.005148000	0.865914000	2.078347000
C	4.302778000	3.232609000	3.012150000
H	5.888010000	2.733842000	1.624663000
C	2.391877000	1.745630000	3.055102000
C	3.029312000	2.882982000	3.528284000
H	4.817287000	4.136737000	3.376098000
H	9.802207000	0.896925000	1.860312000
H	2.552890000	3.505553000	4.303690000
N	4.093224000	0.116331000	-0.664033000
N	4.893316000	-0.358112000	-1.634775000
N	6.166921000	-0.247531000	-1.291621000
N	2.411503000	-0.310356000	1.819834000
O	2.003588000	-1.546763000	-0.132958000
H	2.518499000	-0.893531000	-0.696789000
H	2.604349000	-1.162972000	0.853576000
H	1.420324000	1.422164000	3.462725000

IN6

E_e^S = -2553.533539

C	2.865415000	-3.680063000	3.279409000
C	1.738206000	-2.850522000	3.573188000
C	3.768524000	-3.955505000	4.355403000
C	1.525823000	-2.323491000	4.842071000
C	3.543153000	-3.445209000	5.627717000
C	2.416470000	-2.617953000	5.923551000
H	1.041381000	-2.590048000	2.755748000
H	4.623524000	-4.627497000	4.188665000
H	0.666711000	-1.657198000	5.009272000
H	4.231264000	-3.703422000	6.451891000
N	2.999833000	-4.225154000	2.008624000
C	4.244352000	-4.570258000	1.483227000
C	5.445406000	-3.860714000	1.782530000
C	4.332926000	-5.626793000	0.530812000
C	6.652756000	-4.197370000	1.166431000
C	5.541801000	-5.971310000	-0.077368000
C	6.716512000	-5.254327000	0.231723000
H	5.410739000	-3.001778000	2.468397000
H	3.416139000	-6.187151000	0.283941000
H	7.559662000	-3.613597000	1.399319000
H	5.569255000	-6.798719000	-0.801358000
N	2.246946000	-2.126767000	7.206770000
C	1.009891000	-1.693769000	7.718903000
C	0.947264000	-0.580522000	8.597226000
C	-0.194302000	-2.403787000	7.454830000
C	-0.261977000	-0.191229000	9.190637000
C	-1.400498000	-1.999501000	8.042884000
C	-1.447821000	-0.894674000	8.913675000
H	1.875016000	-0.010531000	8.792723000
H	-0.168157000	-3.290545000	6.804273000
H	-0.278057000	0.678590000	9.866568000
H	-2.318057000	-2.568735000	7.824553000
H	-2.399729000	-0.586867000	9.372810000
Cu	1.469095000	-4.424353000	0.96887300
Cu	3.730142000	-1.653605000	8.21554000
N	8.003579000	-5.610435000	-0.337707000
C	8.011390000	-6.038174000	-1.738762000
C	7.941245000	-7.405474000	-2.060696000
C	8.096287000	-5.071157000	-2.758103000
C	7.952197000	-7.804591000	-3.408774000
C	8.119214000	-5.477569000	-4.102485000
C	8.043744000	-6.843338000	-4.429887000
H	7.891989000	-8.150764000	-1.249104000
H	8.138800000	-4.000408000	-2.500515000
H	7.898746000	-8.875599000	-3.658393000
H	8.191956000	-4.719939000	-4.898166000
H	8.059423000	-7.158954000	-5.484581000
H	8.620158000	-4.787607000	-0.249765000
Cu	9.064578000	-6.910139000	0.83723000
C	-1.791379000	-0.203245000	2.628583000
C	-2.683829000	-1.206190000	2.173755000
C	-2.157210000	0.675457000	3.656984000
C	-3.959541000	-1.304665000	2.780487000
C	-2.168040000	-2.105687000	1.066487000
C	-3.425027000	0.563562000	4.259634000
H	-1.453976000	1.456155000	3.990021000
C	-4.318782000	-0.427072000	3.817708000
H	-4.657219000	-2.069320000	2.408479000
H	-3.715195000	1.251802000	5.070276000
H	-5.314178000	-0.517711000	4.282182000
O	-0.960828000	-2.019665000	0.760131000
C	-3.048792000	-3.040777000	0.339871000
C	-2.817170000	-3.805182000	-0.869616000
C	-1.684204000	-4.024044000	-1.761733000
C	-1.914958000	-4.012522000	-3.161419000
C	-0.337109000	-4.319667000	-1.295490000
C	-0.877353000	-4.193174000	-4.078200000
H	-2.946662000	-3.839151000	-3.500993000
C	0.717240000	-4.464451000	-2.262645000
C	0.453628000	-4.403846000	-3.621421000
H	-1.087899000	-4.159544000	-5.158783000
H	-0.806981000	-0.132908000	2.141001000
H	1.272161000	-4.529271000	-4.348051000
N	-4.016790000	-4.363535000	-1.216013000
N	-4.905513000	-4.008499000	-0.279802000
N	-4.382866000	-3.188740000	0.610918000
N	-0.077697000	-4.492448000	0.017567000
H	-0.940474000	-4.405977000	0.576322000
H	1.735919000	-4.654709000	-1.886673000

IN7

E_e^S = -872.7441284

C	-1.738285000	-0.909383000	3.061465000
C	-2.693885000	-1.681146000	2.352728000
C	-2.145231000	0.063515000	3.981523000
C	-4.071585000	-1.451229000	2.588801000
C	-2.145972000	-2.681176000	1.375019000
C	-3.517437000	0.284970000	4.209927000
H	-1.391909000	0.655136000	4.525738000
C	-4.473954000	-0.473739000	3.513270000
H	-4.816562000	-2.059569000	2.058152000
H	-3.839978000	1.051138000	4.933383000
H	-5.547887000	-0.304506000	3.690799000
O	-0.914602000	-2.737998000	1.191841000
C	-3.020377000	-3.592518000	0.599473000
C	-2.712963000	-4.277051000	-0.609944000
C	-1.615692000	-4.391335000	-1.589813000
C	-1.943629000	-4.192449000	-2.957237000
C	-0.289989000	-4.829278000	-1.246546000
C	-1.022480000	-4.422136000	-3.984775000
H	-2.952851000	-3.825252000	-3.206920000

C	0.622237000	-5.073961000	-2.311283000
C	0.267059000	-4.881046000	-3.648025000
H	-1.302067000	-4.241494000	-5.033546000
H	-0.672942000	-1.099269000	2.862229000
H	1.009482000	-5.076070000	-4.438549000
N	-3.895819000	-4.912090000	-0.875395000
N	-4.853637000	-4.678687000	0.054807000
N	-4.328553000	-3.880269000	0.935647000
N	0.063939000	-5.072047000	0.063484000
H	-0.295591000	-4.345910000	0.715060000
H	1.638345000	-5.418685000	-2.057162000
H	1.062194000	-5.252295000	0.199320000
H	-4.082325000	-5.546627000	-1.657690000

TS5

E_e^S = -872.6957634

C	-2.479889000	-1.178478000	3.695294000
C	-2.700422000	-2.333793000	2.899357000
C	-2.624935000	-1.236014000	5.086631000
C	-3.062406000	-3.548502000	3.539097000
C	-2.518205000	-2.242137000	1.441933000
C	-2.989068000	-2.445463000	5.709306000
H	-2.456604000	-0.332135000	5.693352000
C	-3.206297000	-3.598890000	4.931256000
H	-3.234460000	-4.450731000	2.935508000
H	-3.102972000	-2.490115000	6.804275000
H	-3.490169000	-4.545828000	5.416730000
O	-2.288171000	-1.011880000	0.955771000
C	-3.096883000	-3.282807000	0.570112000
C	-2.578394000	-3.957205000	-0.564990000
C	-1.227953000	-4.132602000	-1.059431000
C	-0.914716000	-5.017010000	-2.122986000
C	-0.155483000	-3.497795000	-0.325508000
C	0.408428000	-5.314457000	-2.458000000
H	-1.726264000	-5.489241000	-2.701119000
C	1.186677000	-3.884419000	-0.642269000
C	1.461539000	-4.752709000	-1.696556000
H	0.627654000	-5.993617000	-3.295792000
H	-2.201447000	-0.243160000	3.188693000
H	2.507201000	-5.001530000	-1.939426000
N	-3.670812000	-4.667877000	-0.998357000
N	-4.756787000	-4.492447000	-0.202099000
N	-4.411160000	-3.675980000	0.751064000
N	-0.473798000	-2.550838000	0.596583000
H	-1.466283000	-1.255595000	0.373177000
H	2.009061000	-3.438408000	-0.059029000
H	0.312258000	-2.356458000	1.237293000
H	-3.732739000	-5.313622000	-1.787958000

IN8

E_e^S = -872.750296

C	-2.845744000	-1.196748000	3.306126000
C	-2.179855000	-2.301366000	2.739212000
C	-3.104437000	-1.160259000	4.686495000
C	-1.787843000	-3.371577000	3.568844000
C	-1.933735000	-2.360832000	1.222952000
C	-2.704686000	-2.225311000	5.512458000
H	-3.624450000	-0.290959000	5.119883000
C	-2.046231000	-3.332394000	4.949457000
H	-1.278206000	-4.241478000	3.125845000
H	-2.908803000	-2.194233000	6.594728000
H	-1.733046000	-4.173862000	5.588021000
O	-1.895763000	-1.002407000	0.763508000
C	-2.994984000	-3.140909000	0.487419000
C	-2.707951000	-4.030938000	-0.553706000
C	-1.370123000	-4.380906000	-0.974453000
C	-1.026330000	-5.201078000	-2.071990000
C	-0.338400000	-3.813200000	-0.153659000
C	0.313048000	-5.475898000	-2.373462000
H	-1.826704000	-5.625949000	-2.699464000
C	1.012557000	-4.099552000	-0.476818000
C	1.327981000	-4.919964000	-1.566233000
H	0.569515000	-6.115791000	-3.231013000
H	-3.153345000	-0.370052000	2.651354000
H	2.385860000	-5.126380000	-1.793802000
N	-3.950368000	-4.420227000	-0.970955000
N	-4.934321000	-3.811799000	-0.241171000
N	-4.350331000	-3.036099000	0.635484000
N	-0.659523000	-3.046455000	0.955099000
H	-2.048637000	-1.025655000	-0.201623000
H	1.816023000	-3.670445000	0.143899000
H	0.130452000	-2.634453000	1.458201000
H	-4.210965000	-5.085030000	-1.702128000

TS6

E_e^S = -872.695882

C	-0.785099000	-2.622116000	3.889574000
C	-1.913813000	-2.955390000	3.105409000
C	-0.937890000	-2.248067000	5.234016000
C	-3.198339000	-2.930102000	3.701545000
C	-1.730427000	-3.337964000	1.671583000
C	-2.216646000	-2.211330000	5.816692000
H	-0.049311000	-1.993289000	5.833505000
C	-3.342640000	-2.556757000	5.045824000
H	-4.075886000	-3.217676000	3.104680000
H	-2.336217000	-1.922188000	6.873058000
H	-4.346790000	-2.539707000	5.498714000

O	-2.041118000	-1.531028000	0.911584000
C	-2.547422000	-4.357032000	1.043929000
C	-2.072583000	-5.072623000	-0.074106000
C	-0.777141000	-4.862313000	-0.656470000
C	-0.249795000	-5.537527000	-1.785188000
C	-0.014274000	-3.828225000	-0.008423000
C	1.001186000	-5.189858000	-2.297374000
H	-0.838510000	-6.334181000	-2.268493000
C	1.249838000	-3.484661000	-0.560879000
C	1.742847000	-4.151668000	-1.682822000
H	1.405642000	-5.715287000	-3.175761000
H	0.212828000	-2.673137000	3.428918000
H	2.727201000	-3.870475000	-2.089733000
N	-3.103095000	-5.917038000	-0.358137000
N	-4.150572000	-5.739254000	0.513693000
N	-3.811281000	-4.808188000	1.353729000
N	-0.453706000	-3.160210000	1.123242000
H	-0.723235000	-2.011750000	0.991919000
H	1.833770000	-2.689265000	-0.072947000
H	-2.320883000	-0.905488000	1.614393000
H	-3.185042000	-6.618841000	-1.096434000

3a

E_e^S = -796.3229791

C	-1.084976000	-2.282780000	3.693682000
C	-1.945486000	-3.274226000	3.157894000
C	-1.374134000	-1.673858000	4.920702000
C	-3.104899000	-3.638048000	3.886976000
C	-1.599862000	-3.895163000	1.851251000
C	-2.528426000	-2.041687000	5.639113000
H	-0.695234000	-0.905105000	5.323532000
C	-3.388499000	-3.023217000	5.117183000
H	-3.779498000	-4.405406000	3.480348000
H	-2.755935000	-1.562224000	6.604861000
H	-4.293315000	-3.316187000	5.673305000
C	-2.404056000	-4.912663000	1.206410000
C	-1.992831000	-5.444014000	-0.037862000
C	-0.800892000	-5.015563000	-0.696825000
C	-0.307441000	-5.486676000	-1.941535000
C	-0.079643000	-3.999391000	0.038559000
C	0.878363000	-4.971925000	-2.463220000
H	-0.861878000	-6.260614000	-2.496902000
C	1.129321000	-3.499053000	-0.530796000
C	1.596678000	-3.974853000	-1.752760000
H	1.258485000	-5.339568000	-3.429071000
H	-0.189484000	-2.011636000	3.115408000
H	2.532528000	-3.575121000	-2.174249000
N	-2.968676000	-6.351732000	-0.331752000
N	-3.920249000	-6.390489000	0.652158000
N	-3.585881000	-5.533605000	1.569586000
N	-0.486918000	-3.489216000	1.245366000
H	1.671263000	-2.726183000	0.034810000
H	-3.067402000	-6.965815000	-1.142415000

TS1'

E_e^S = -4909.208852

C	-0.213019000	0.913622000	-0.558941000
C	1.163309000	0.715500000	-0.258219000
C	-0.648046000	2.262449000	-0.718975000
C	2.048924000	1.784117000	-0.103257000
C	0.241572000	3.329711000	-0.582188000
C	1.613182000	3.129119000	-0.266442000
H	1.526623000	-0.319561000	-0.122076000
H	-1.692805000	2.465527000	-0.998553000
H	3.101370000	1.587311000	0.152518000
H	-0.113140000	4.362084000	-0.737712000
N	-1.048973000	-0.192821000	-0.756006000
C	-2.416342000	-0.158490000	-0.493016000
C	-3.005256000	0.667627000	0.512139000
C	-3.292797000	-1.040842000	-1.191505000
C	-4.375598000	0.612732000	0.787258000
C	-4.664962000	-1.084623000	-0.922446000
C	-5.226637000	-0.251774000	0.065850000
H	-2.361895000	1.326244000	1.113386000
H	-2.867804000	-1.683273000	-1.982337000
H	-4.797084000	1.228566000	1.599730000
H	-5.310773000	-1.766016000	-1.501249000
N	2.461631000	4.235913000	-0.107955000
C	3.811614000	4.194001000	-0.479124000
C	4.794316000	4.948233000	0.218842000
C	4.242724000	3.474244000	-1.632655000
C	6.124445000	5.007206000	-0.220515000
C	5.577760000	3.527585000	-2.055013000
C	6.534115000	4.292959000	-1.360547000
H	4.485179000	5.483415000	1.137411000
H	3.506239000	2.893862000	-2.208551000
H	6.853439000	5.605680000	0.349991000
H	5.872800000	2.964501000	-2.955833000
H	7.581308000	4.325963000	-1.698661000
Cu	-0.301924000	-1.827264000	-1.249454000
Cu	2.010434000	5.481706000	1.193225000
N	-6.646435000	-0.313142000	0.369596000
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C	-7.085370000	1.918924000	-0.668194000
C	-8.916983000	0.349287000	-0.303438000
C	-8.002095000	2.845111000	-1.196489000
C	-9.820639000	1.279711000	-0.836412000
C	-9.369562000	2.535269000	-1.284279000
H	-6.015014000	2.165055000	-0.615871000
H	-9.277817000	-0.628171000	0.057728000

H	-7.633500000	3.821452000	-1.549266000
H	-10.889002000	1.019209000	-0.899923000
H	-10.080774000	3.265824000	-1.699460000
H	-6.999285000	-1.253779000	0.138795000
Cu	-6.982479000	-0.388273000	2.433824000
C	7.552352000	-1.922852000	-0.184480000
C	6.422300000	-2.175831000	0.630232000
C	8.794034000	-1.618635000	0.386744000
Br	0.481515000	-3.880453000	-2.086608000
C	6.572385000	-2.116496000	2.036101000
C	5.127015000	-2.494363000	-0.069678000
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H	5.716739000	-2.306899000	2.701121000
H	9.906865000	-1.322146000	2.238938000
H	7.920085000	-1.769025000	3.705188000
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C	2.723071000	-3.013105000	0.113996000
H	2.777450000	-3.013863000	-0.988802000
C	1.433169000	-3.303288000	0.723668000
C	1.262691000	-3.430199000	2.134462000
C	0.239429000	-3.484272000	-0.038576000
C	0.033143000	-3.736846000	2.720999000
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H	-1.878132000	-4.001267000	-0.120402000
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IN2’

E_e^S = -4909.255777

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Cu	1.076360000	-4.224447000	-1.701909000
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N	2.268466000	0.282070000	-6.291159000
C	3.399490000	-0.182711000	-7.082977000
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H	4.858278000	0.947346000	-5.933345000
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C	-3.385917000	-6.805851000	2.549007000
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C	-5.355201000	-8.207667000	2.936197000
H	-4.559668000	-7.766820000	0.972425000
H	-5.936862000	-8.500581000	5.013948000
H	-6.172678000	-8.829418000	2.537499000
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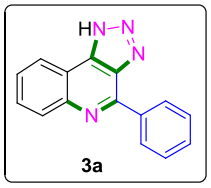
H	-3.453291000	-6.567346000	-2.423456000	H	-2.417881000	-6.027035000	4.311819000

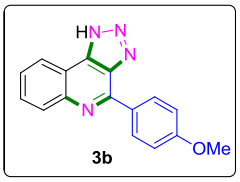
14. Spectroscopic data of triazolo quinolines and triazolyl benzamide derivatives

4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3a)**: Purified by column chromatography, Light yellow solid,



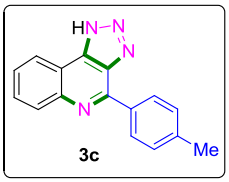
^{1}H NMR (500 MHz, DMSO-d_6) 8.86 (d. J = 7 Hz, 2H), 8.42 (d, J = 7.5 Hz, 1H), 8.25 (d, J = 8 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1 H), 7.79, (t, J = 7.25 Hz, 1H), 7.67 – 7.60 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.4, 142.8, 141.7, 135.8, 135.2, 135.0, 134.5, 133.9, 133.6, 132.9, 132.7, 128.0, 127.9. HRMS calcd for $C_{15}H_{10}N_4$ [M+H] 247.0939; found, 247.0977. [S5]

4-(4-methoxyphenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3b)**: Purified by column chromatography,



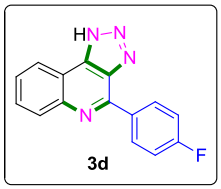
White solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (d, J = 7.2 Hz, 2H), 8.53, (d, J = 7.6 Hz, 1H), 8.35 (d, J = 7.4 Hz, 1H), 7.98 (t, J = 7.2 Hz, 1H), 7.88 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 8.8 Hz, 2H), 4.03 (s,3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.8, 149.6, 144.7, 131.4, 130.2, 130.0, 129.5, 127.4, 123.2, 114.6, 55.8. HRMS calcd for $C_{16}H_{12}N_4O$ [M+H] 277.1045; found, 277.1088. [S5]

4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3c)**: Purified by column chromatography, White solid, ^{1}H



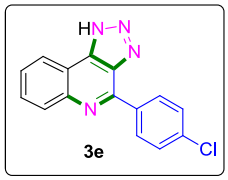
NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 2H), 8.42 (d, J = 7.6 Hz, 1H), 8.25 (d, J = 8 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.6, 144.6, 140.9, 134.3, 130.6, 130.3, 130.1, 129.7, 129.7, 127.7, 123.2, 21.6. HRMS calcd for $C_{16}H_{12}N_4$ [M+H] 261.1096; found, 261.1136. [S5]

4-(4-fluorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3d)**: Purified by column chromatography, White

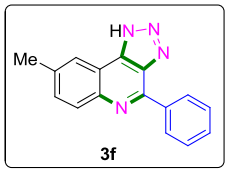


solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.95 (t, J = 7 Hz, 2H), 8.41 (d, J = 8 Hz, 1H), 8.23 (d, J = 8 Hz, 1H), 7.87 (t, J = 7.75 Hz, 1H), 7.78 (t, J = 7.25 Hz, 1H), 7.49 (t, J = 8.75 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 163.1, 148.6, 144.4, 133.4, 133.4, 132.0, 131.9, 130.3, 130.1, 127.8, 123.2, 116.1, 116.0. HRMS calcd for $C_{15}H_9N_4F$ [M+H] 265.0845; found, 265.0885. [S5]

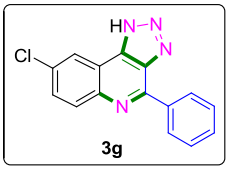
4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3e)**: Purified by column chromatography, White solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 2H), 8.42 (d, J = 7.2 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 7.2 Hz, 1H), 7.81 (t, J = 7.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.6, 144.4, 137.9, 135.9, 135.7, 131.4, 130.5, 130.2, 129.2, 128.2, 123.3, 115.1. HRMS calcd for $C_{15}H_9N_4Cl$ [M+H] 282.0486, found, 281.0587. [S5]



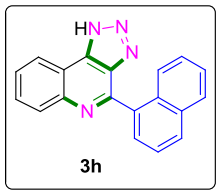
8-methyl-4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3f)**: Purified by column chromatography, White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.87 (d, J = 6.5 Hz, 2H), 8.22 (s, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.63 (d, J = 7 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.0, 142.9, 137.7, 137.0, 130.8, 130.0, 129.6, 129.1, 122.4, 115.6, 21.8. HRMS calcd for $C_{16}H_{12}N_4$ [M+H] 261.1096; found, 261.1130. [S6]



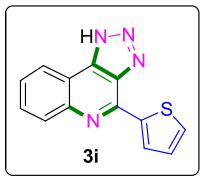
8-chloro-4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3g)**: Purified by column chromatography, White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.79 (s, 2H), 8.36 (d, J = 2.5 Hz, 1H), 8.17 (d, J = 9 Hz, 1H), 7.79 (dd, J = 2.5 Hz, 9 Hz, 1H), 7.65 – 7.58 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.3, 142.9, 136.6, 132.1, 132.0, 131.2, 130.4, 129.7, 129.1, 122.3. HRMS calcd for $C_{15}H_9N_4Cl$ [M+H] 282.0486; found, 281.0586. [S6]



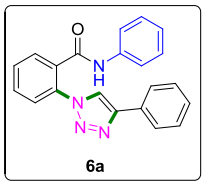
4-(naphthalen-1-yl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3h)**: Purified by column chromatography, Yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.26 (d, J = 8 Hz, 1H), 8.16 (d, J = 8Hz, 1H), 8.08 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 7.2 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.0, 144.6, 134.5, 133.9, 132.0, 131.4, 130.3, 130.2, 129.5, 129.1, 128.8, 127.1, 126.6, 126.2, 125.7, 123.3. HRMS calcd for $C_{19}H_{12}N_4$ [M+H] 297.1096; found, 297.1132 [S6]



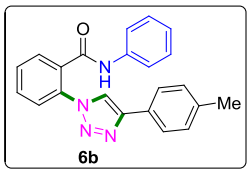
4-(thiophen-2-yl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline **(3i)**: Purified by column chromatography, Brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 (d, J = 2.5 Hz, 1H), 8.40 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 5 Hz, 1H), 7.85 (t, 7.5 Hz, 1H), 7.76 (t, J = 7.25 Hz, 1H), 7.40 (t, J = 4.25 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 156.1, 145.6, 144.6, 143.4, 143.2, 142.0, 132.0, 131.3, 130.4, 129.6, 129.3, 129.3, 128.8, 127.6, 115.7, 112.5. HRMS calcd for $C_{13}H_8N_4S$ [M+H] 253.0503; found, 253.0543 [S6]



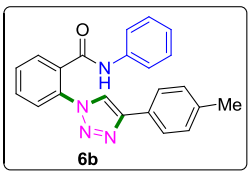
N-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide **(6a)**: Purified by column chromatography, Yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.20 (s, 1H), 8.12 (s, 1H), 7.87 – 7.81 (m, 3H), 7.63 – 7.62 (m, 2H), 7.56 – 7.55 (m, 1H), 7.47 – 7.42 (m, 4H), 7.38 – 7.35 (m, 1H), 7.27 (t, J = 8.5 Hz, 2H), 7.10 (t, J = 9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.3, 148.4, 137.3, 133.8, 133.0, 131.4, 130.3, 129.7, 129.0, 128.9, 128.6, 126.3, 125.9, 126.0, 122.1, 120.4. HRMS calcd for $C_{21}H_{16}N_4O$ [M+H] 341.1358; found 341.1402. [S7]



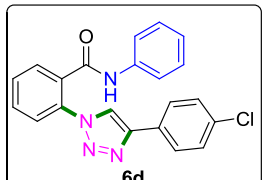
N-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide **(6b)**: Purified by column chromatography, White solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (s, 1H), 8.08 (s, 1H), 7.83 -7.81 (m, 1H), 7.67 (d, J = 10 Hz, 2H), 7.59 – 7.57 (m, 2H), 7.51 – 7.49 (m, 1H), 7.43 (d, J = 10 Hz, 2H), 7.26 – 7.20 (m, 4H), 7.07 (t, J = 9.25 Hz, 1H), 2.37 (s.1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164. 3, 148.5, 138.5, 137.3, 133.8, 132.9, 131.4, 130.2, 129.8, 129.6, 128.9, 126.9, 126.3, 125.9, 124.9, 121.7, 120.4, 21.3. HRMS calcd for $C_{22}H_{18}N_4NaO$ $[M+Na]^+$ 378.1412; found 377.1370.



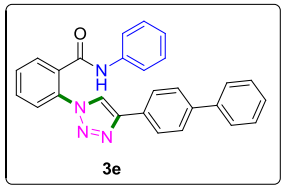
2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide **(6c)**: Purified by column chromatography, Light pink solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.55 (s, 1H), 9.00 (s, 1H), 7.95 (q, J = 5.5 Hz, 8.5 Hz, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.76 (d, J = 4 Hz, 2H), 7.73 – 7.70 (m, 1H), 7.59 (d, J = 8 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.07 (t, J = 7.25 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 163.4, 161.4, 146.1, 139.4, 134.6, 133.4, 131.5, 130.1, 129.6, 129.1, 127.8, 127.8, 127.4, 127.3, 125.6, 124.2, 122.9, 120.2, 116.5, 116.3. HRMS calcd for $C_{21}H_{15}FN_4NaO$ $[M+Na]^+$ 382.1161; found 381.1107.



2-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide **(6d)**: Purified by column chromatography, Yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 1H), 9.06 (s, 1H), 7.94 – 7.92 (m, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.73 – 7.70 (m, 1H), 7.59 – 7.54 (m, 4H), 7.29 (t, J = 8 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 145.9, 139.4, 134.5, 133.4, 133.0, 131.5, 130.1, 129.7, 129.6, 129.5, 129.1, 127.4, 125.7, 124.2, 123.3, 120.2. HRMS calcd for $C_{21}H_{15}ClN_4NaO$ $[M+Na]^+$ 399.0803; found 397.0826.

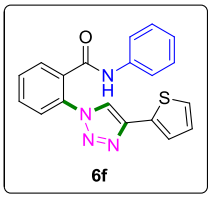


2-(4-([1,1'-biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide **(6e)**: Purified by column chromatography, Whitish solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.57 (s, 1H), 9.07 (s, 1H), 8.01 (d, J = 8 Hz, 2H), 7.83 – 7.77 (m, 6H), 7.75 – 7.72 (m, 2H), 7.61 (d, J = 8 Hz, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.25 Hz, 1H), 7.31 (t, J = 7.75 Hz, 2H), 7.07 (t, J = 7.25 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ



165.2, 146.7, 140.2, 140.0, 139.5, 134.6, 133.4, 131.5, 130.1, 129.9, 129.7, 129.5, 129.1, 128.1, 127.7, 127.0, 126.3, 125.6, 124.2, 123.0, 120.2. HRMS calcd for $C_{27}H_{20}N_4NaO$ $[M+Na]^+$ 440.1768; found 439.1530.

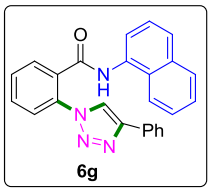
N-phenyl-2-(4-(thiophen-2-yl)-1*H*-1,2,3-triazol-1-yl)benzamide **(6f)**: Purified by column chromatography,



6f

Brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.55 (s, 1H), 8.91 (s, 1H), 7.81 (d, J = 7 Hz, 1H), 7.77 – 7.76 (m, 2H), 7.72 – 7.69 (m, 1H), 7.61 – 7.56 (m, 3H), 7.51 (d, J = 3 Hz, 1H), 7.30 (t, J = 7.75 Hz, 2H), 7.16 (t, J = 4.25 Hz, 1H), 7.07 (t, 7.25 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 142.4, 139.4, 134.4, 133.4, 132.9, 131.5, 130.2, 129.6, 129.1, 128.4, 126.2, 125.7, 125.0, 124.2, 122.2, 120.2. HRMS calcd for $C_{19}H_{14}N_4NaOS$ $[M+Na]^+$ 370.0820; found 369.0779.

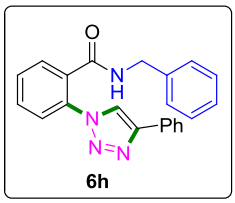
N-(naphthalen-1-yl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide **(6g)**: Purified by column



6g

chromatography, Yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.55 (s, 1H), 9.05 (s, 1H), 7.99 – 7.91 (m, 6H), 7.81 – 7.76 (m, 4H), 7.52 – 7.47 (m, 4H), 7.42 – 7.35 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.2, 147.1, 134.7, 134.1, 133.6, 131.4, 130.8, 130.1, 129.8, 129.4, 129.0, 128.6, 128.4, 126.5, 126.5, 126.2, 125.9, 125.8, 125.7, 123.7, 123.3, 123.2. HRMS calcd for $C_{25}H_{18}N_4NaO$ $[M+Na]^+$ 414.1412; found 413.1375.

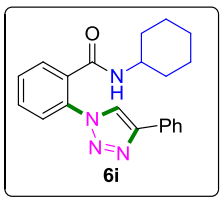
N-benzyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide **(6h)**: Purified by column chromatography, Light



6h

brown solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.05 (s, 1H), 8.82 (s, 1H), 7.91 (s, 2H), 7.70 (s, 4H), 7.49 (s, 2H), 7.38 (s, 1H), 7.22 (s, 5H), 4.35 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.6, 146.9, 139.4, 134.6, 133.5, 131.2, 130.9, 129.4, 129.3, 128.7, 128.6, 127.6, 127.2, 126.1, 125.8, 123.2. HRMS calcd for $C_{22}H_{18}N_4NaO$ $[M+Na]^+$ 378.1412; found 377.1382.

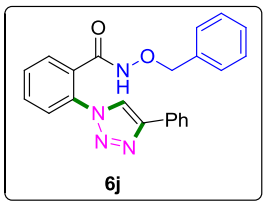
N-cyclohexyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide **(6i)**: Purified by column chromatography,



6i

Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (s, 1H), 8.28 (d, J = 8 Hz, 1H), 7.93 – 7.91 (m, 2H), 7.69 – 7.67 (m, 2H), 7.65 – 7.59 (m, 2H), 7.49 (t, J = 7.75 Hz, 2H), 7.37 (t, J = 7.25 Hz, 1H), 3.60 – 3.53 (m, 1H), 1.70 – 1.67 (m, 2H), 1.63 – 1.60 (m, 2H), 1.23 – 1.03 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 146.8, 134.5, 134.1, 130.9, 130.8, 130.0, 129.5, 129.3, 128.5, 125.8, 125.7, 123.1, 48.5, 32.4, 25.6, 25.0. HRMS calcd for $C_{21}H_{22}N_4NaO$ $[M+Na]^+$ 370.1725; found 369.1693.

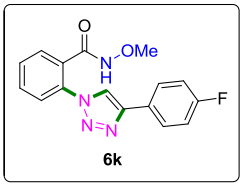
N-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide **(6j)**: Purified by column chromatography,



6j

Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.73 (s, 1H), 8.96 (s, 1H), 6.45 (d, J = 8 Hz, 2H), 7.74 (d, J = 4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.39 – 7.34 (m, 6H), 4.81 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.7, 147.0, 136.2, 135.0, 131.8, 130.8, 130.6, 130.1, 129.8, 129.5, 129.4, 128.8, 128.8, 128.6, 125.8, 123.1, 77.3, 31.2. HRMS calcd for $C_{22}H_{18}N_4NaO_2$ $[M+Na]^+$ 394.1361; found 393.1327.

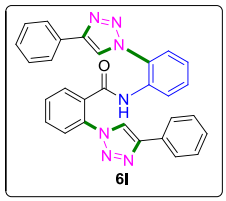
2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-methoxybenzamide **(6k)**: Purified by column



6k

chromatography, Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.63 (s, 1H), 8.93 (s, 1H), 7.98 (q, J = 7 Hz, 10.5 Hz, 2H), 7.74 – 7.73 (m, 2H), 7.67 – 7.64 (m, 2H), 7.49 (t, J = 11 Hz, 2H), 3.58 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.7, 163.3, 161.2, 146.1, 134.9, 131.8, 130.6, 130.2, 129.7, 127.9, 127.8, 127.3, 125.9, 123.0, 116.5, 116.3, 63.4. HRMS calcd for $C_{26}H_{13}FN_4O_2$ [M+2H] 313.1056; found 315.1717.

2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-*N*-(2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)phenyl)benzamide **(6l)**: Purified



6l

by column chromatography, Light yellow solid, ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 1H), 9.04 (d, J = 14 Hz, 2H), 7.96 (dd, J = 7.5 Hz, 18.5 Hz, 4H), 7.77 – 7.66 (m, 6H), 7.59 (t, J = 7.5 Hz, 1H), 7.46 (q, J = 7.5 Hz, 15 Hz, 5 H), 7.35 (q, J = 7.5 Hz, 15.5 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7, 147.2, 147.0, 134.6, 132.5, 131.7, 131.6, 130.9, 130.7, 130.2, 129.9, 129.5, 129.4, 128.6, 128.5, 127.8, 127.2, 126.3, 125.8, 125.8, 125.5, 123.1, 122.9. HRMS calcd for $C_{29}H_{21}N_7NaO$ $[M+Na]^+$ 507.1739; found 506.1716.

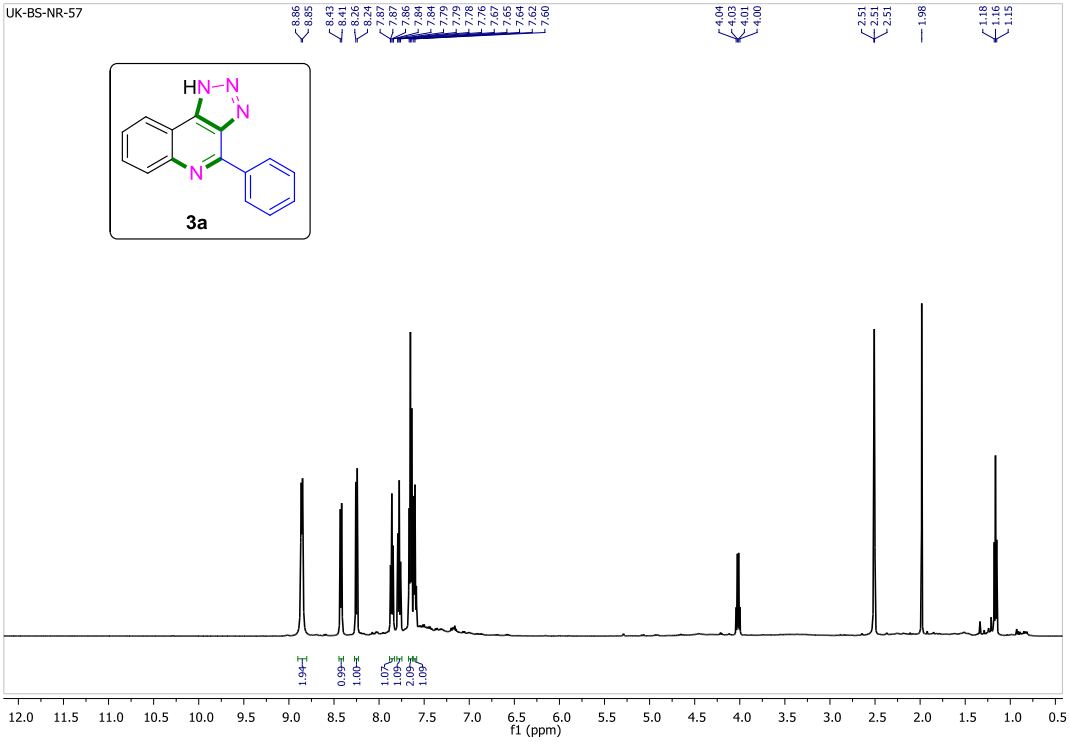
15. References

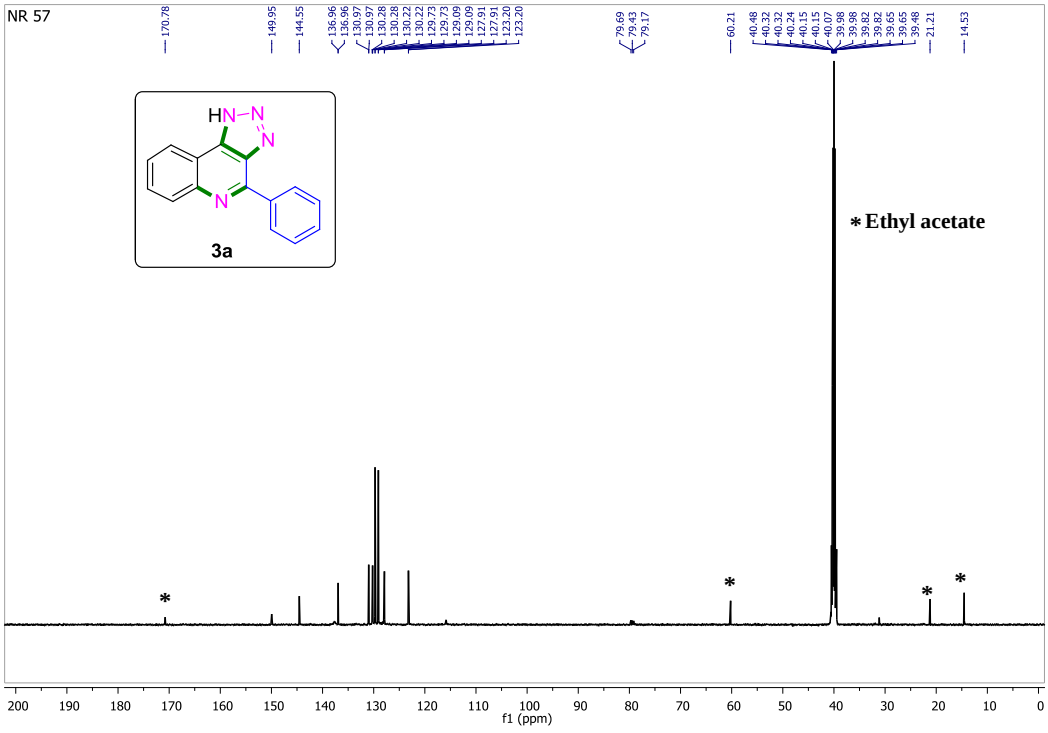
1. M. Rawat, T. Taniike, and D. S. Rawat, *Chem. Cat. Chem.* 2022, **14**, e202101926.
2. T. Wang, L. Zhang, H. Wang, W. Yang, Y. Fu, W. Zhou, W. Yu, K. Xiang, Z. Su, S. Dai, and L. Chai, *ACS Appl. Mater. Interfaces.* 2013, **5**, 12449-12459.
3. Sun, C.; Zhou, R.; Jianan, E.; Sun, J.; Ren, H., *RSC Adv.* **2015,** *5*, 57058-57066.
4. T. Wang, L. Zhang, C. Li, W. Yang, T. Song, C. Tang, Y. Meng, S. Dai, H. Wang, and L. Chai, *Environ. Sci. Technol.* 2015, **49**, 5654-5662.
5. K. Upadhyaya, A. Ajay, R. Mahar, R. Pandey, B. Kumar, S. K. Shukla, and R. P. Tripathi, *Tetrahedron* 2013, **69**, 8547-8558.
6. C. Xu, S. -F. Jiang, Y. -D. Wu, F. -C. Jia, and A.-X. Wu, *J. Org. Chem.*, 2018, **83**, 14802-14810.
7. A. Hayeebueraheng, B. Kaewmee, V. Rukachaisirikul, and J. Kaeobamrung, *Eur. J. Chem.*, 2017, **2017**, 6714-6721.

8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. Gaussian 09, revision D.01; Gaussian,Inc.: Wallingford CT, **2013**.
9. a) A. Becke, *Phys. Rev. A.*, 1988, **38**, 3098-3100; b) J. P. Perdew, *Phys. Rev., B.* 1986, **33**, 8822-8824.
10. F. Weigend, and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297-3305.
11. U. Häussermann, M. Dolg, H. Stoll, H. Preuss, P. Schwerdtfeger, and R. M. Pitzer, *Mol. Phys*., 1993, **78**, 1211-1224.
12. a) K. Fukui, *Acc. Chem. Res.* 1981, **14**, 363–368; b) S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, and K. Morokuma, *Int. J. Quantum Chem.*, 2015, **115**, 258–269; c) C. Gonzalez, and H. B. Schlegel, *J. Phys. Chem.* 1990, **94,** 5523–5527.
13. Y. Zhao, and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
14. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B,* 2009, **113**, 6378-6396.

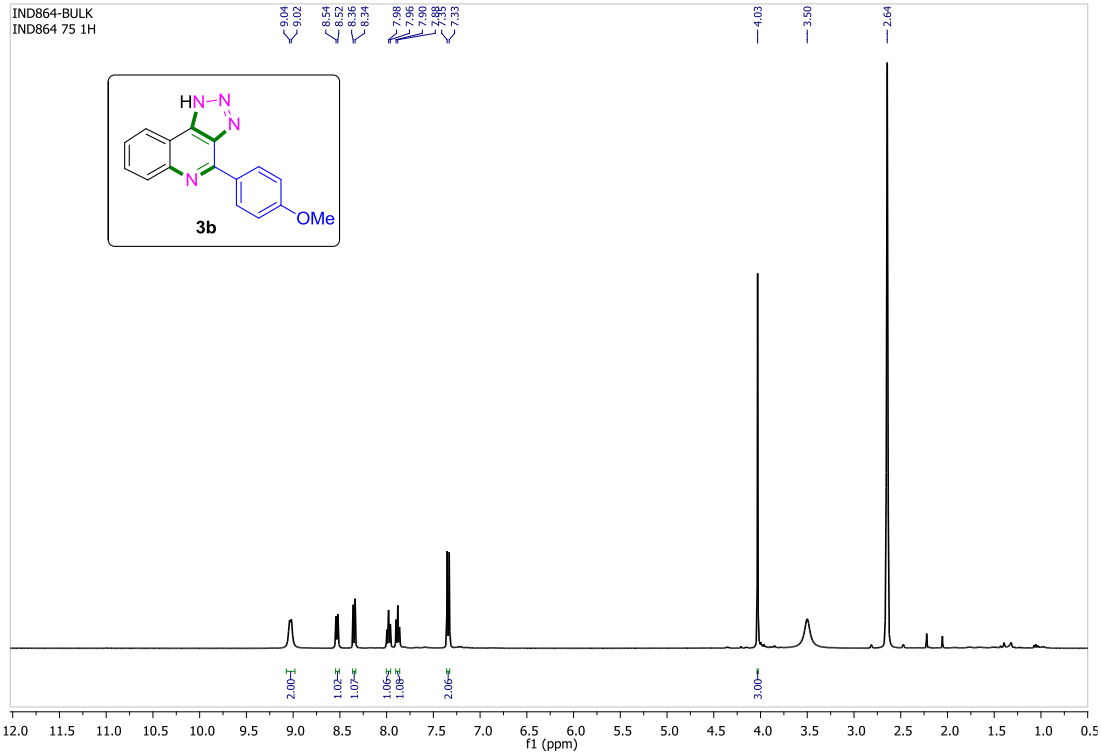
Appendix I: Spectral copies of ^{1}H and ^{13}C NMR of compounds obtained in this study

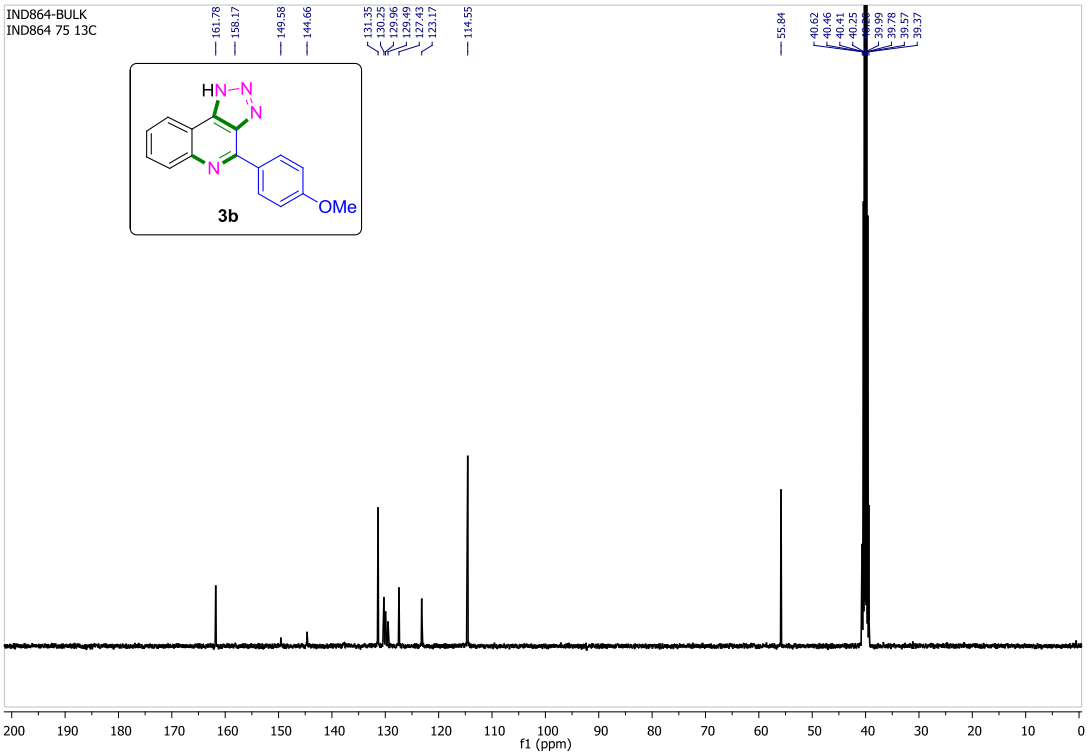
4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3a)



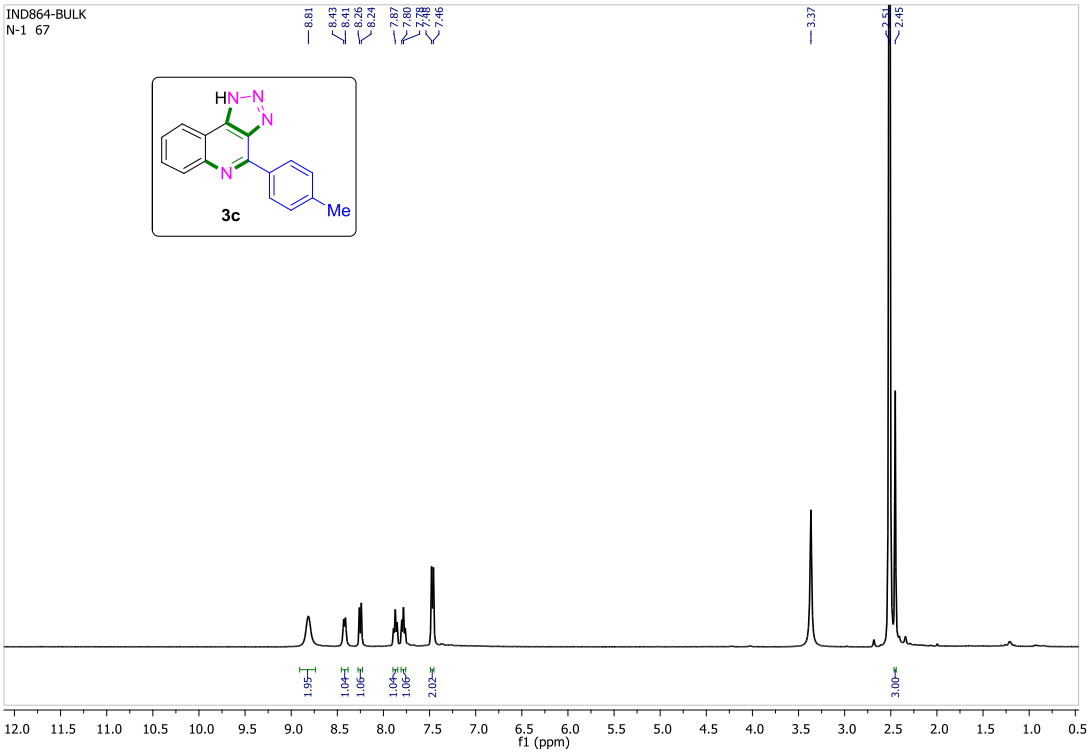


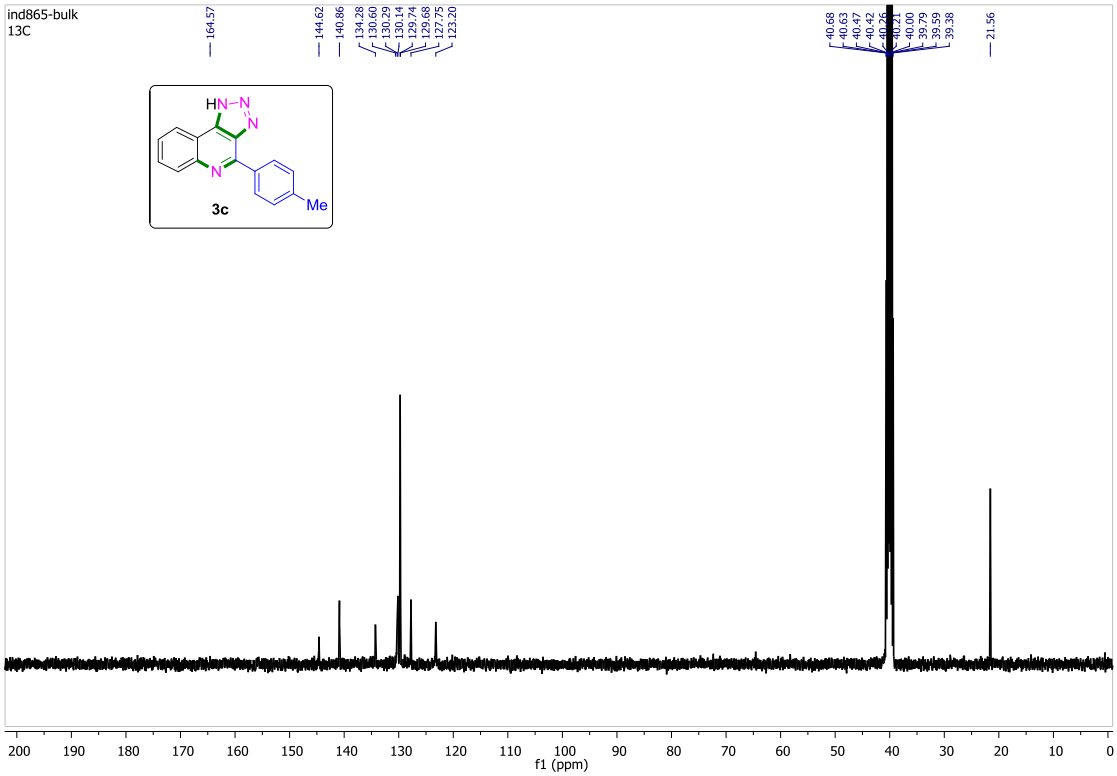
4-(4-methoxyphenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3b)



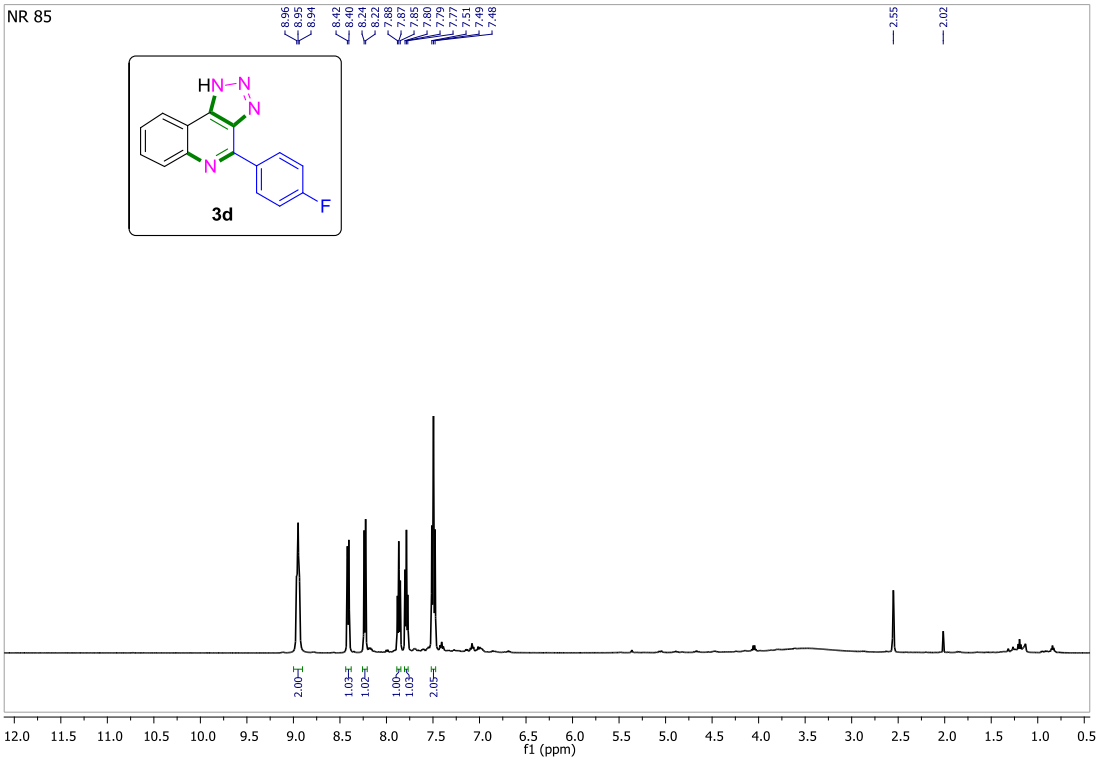


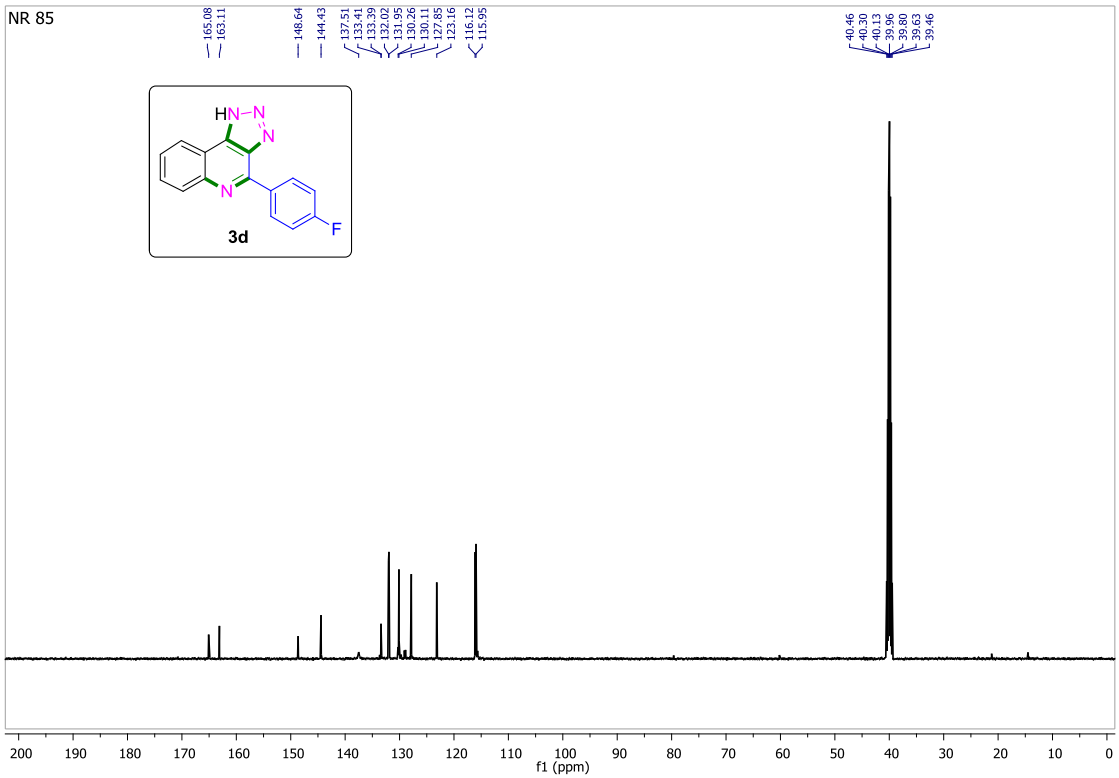
4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3c)



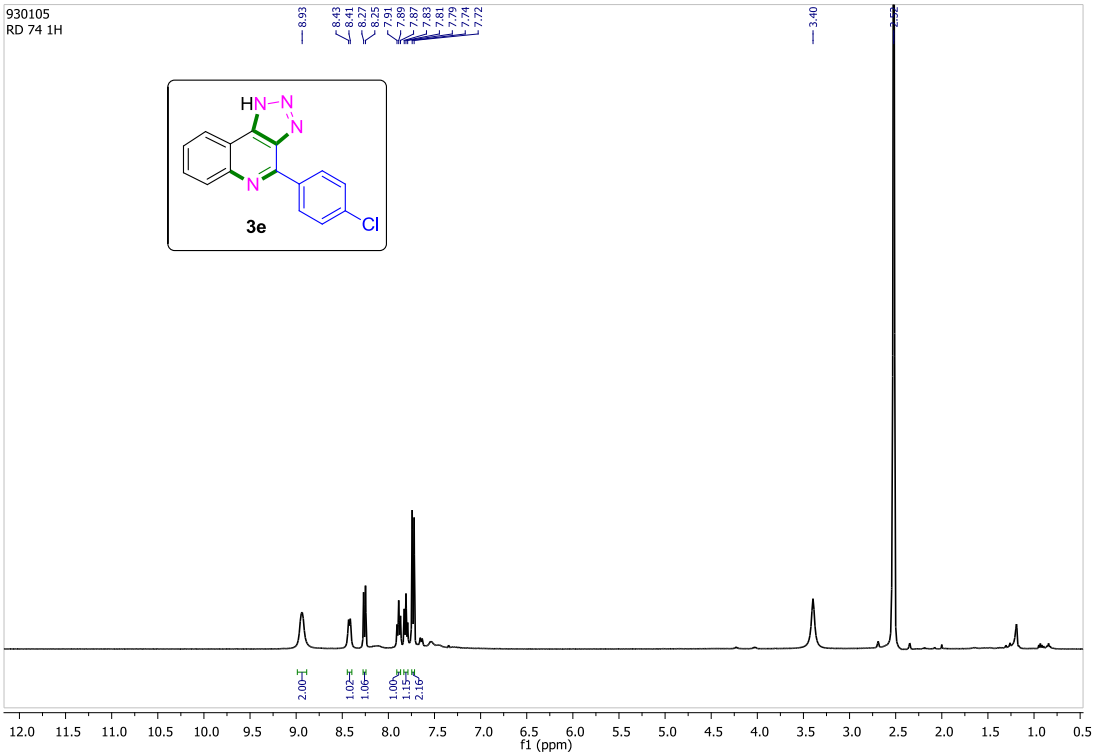


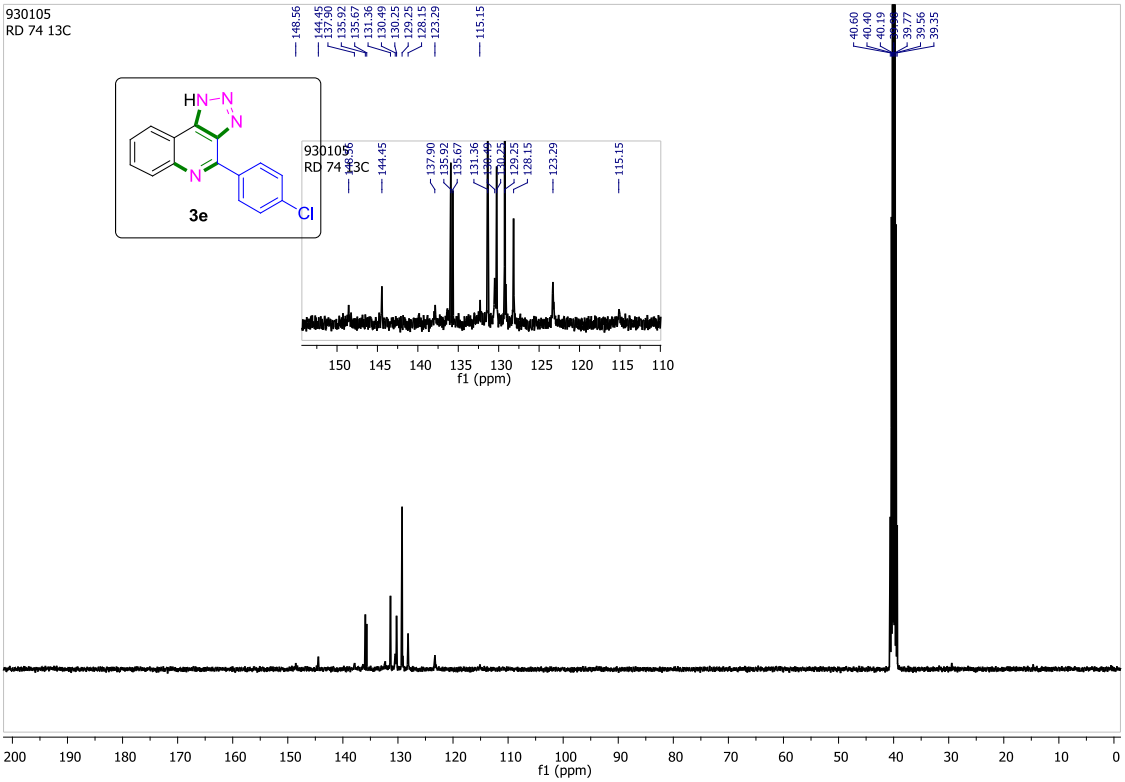
4-(4-fluorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3d)



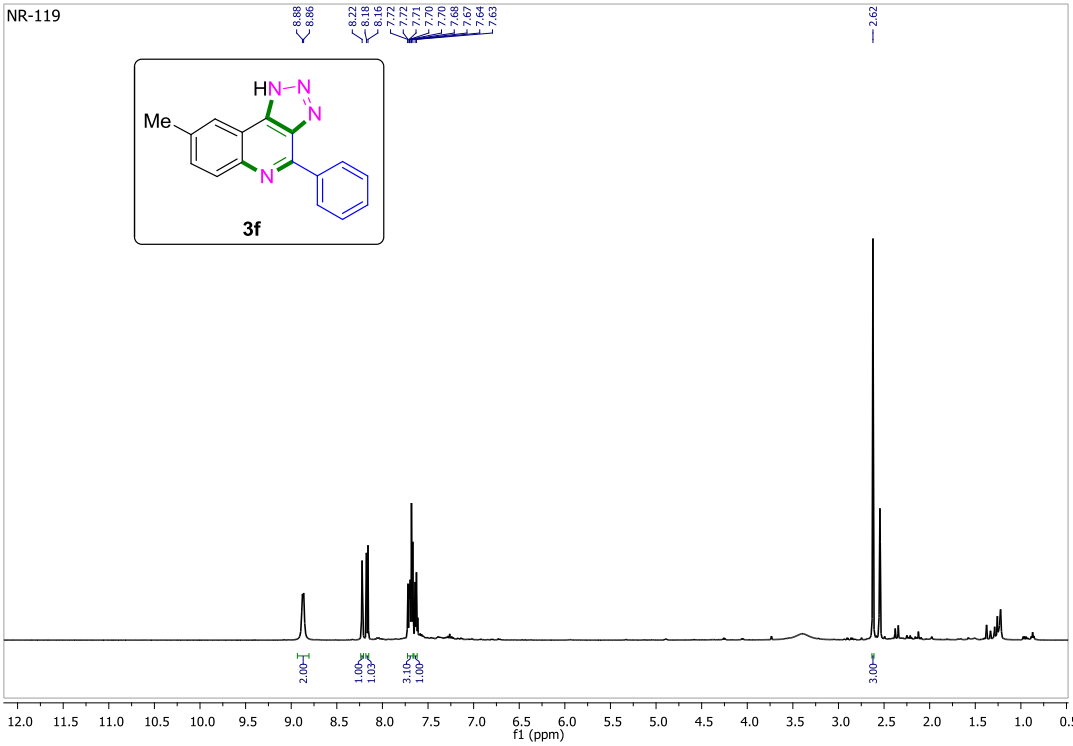


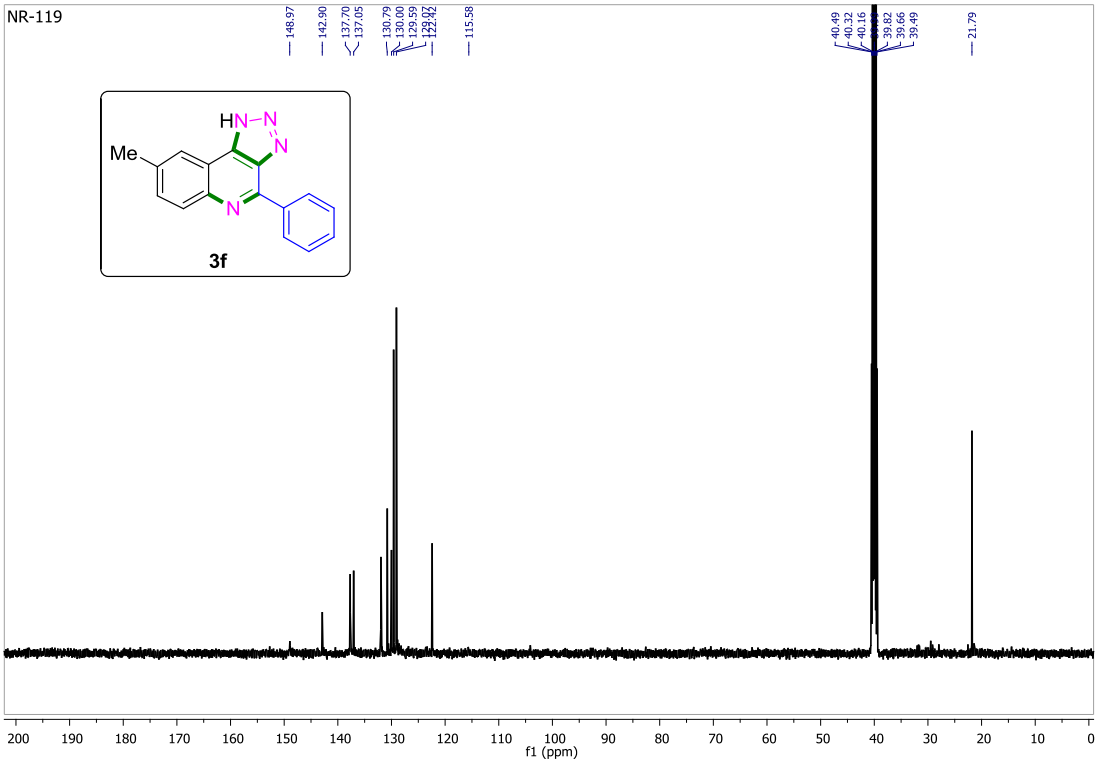
4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3e)



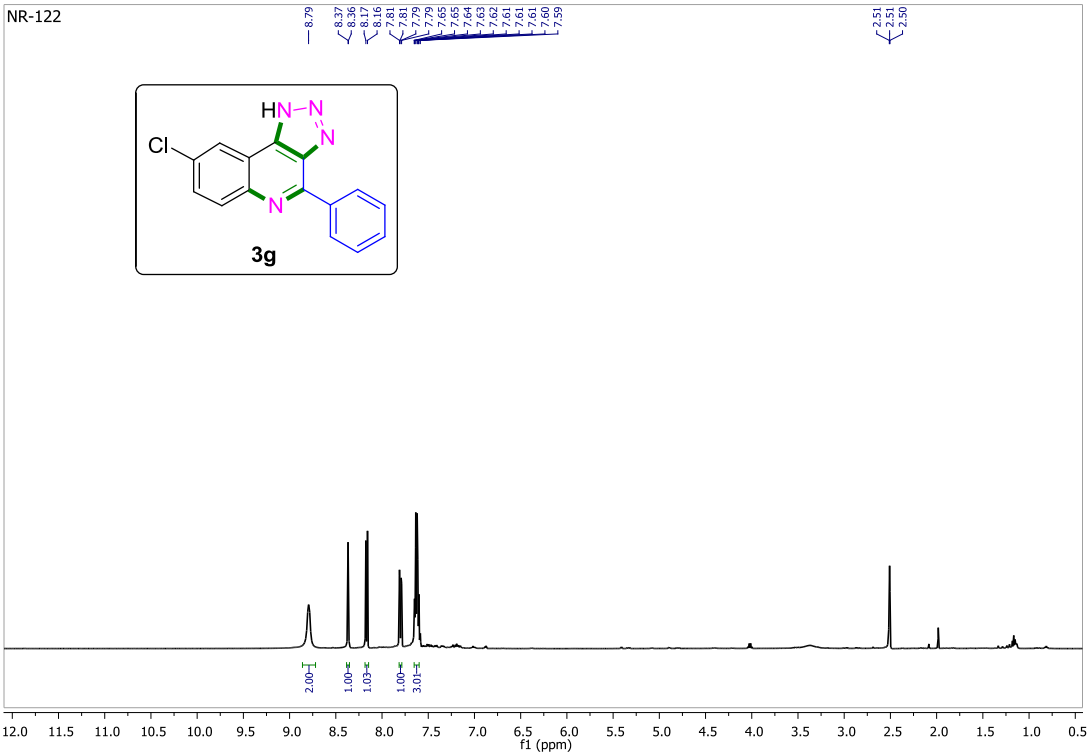


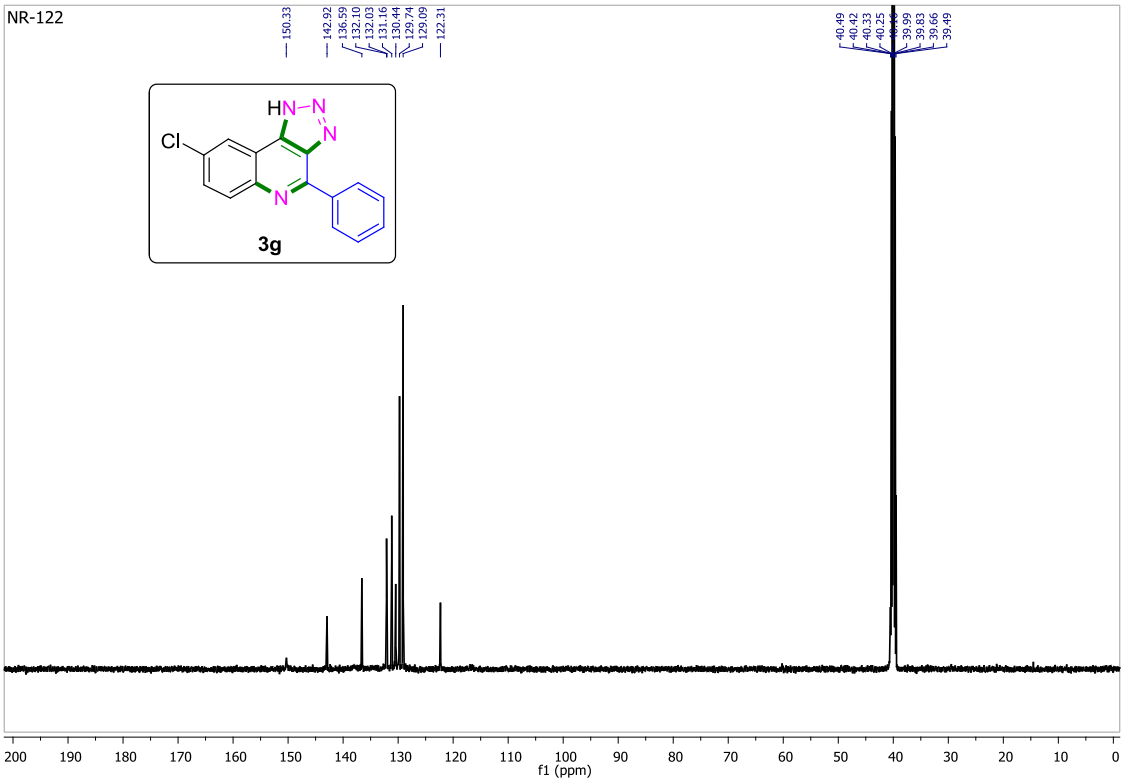
8-methyl-4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3f)



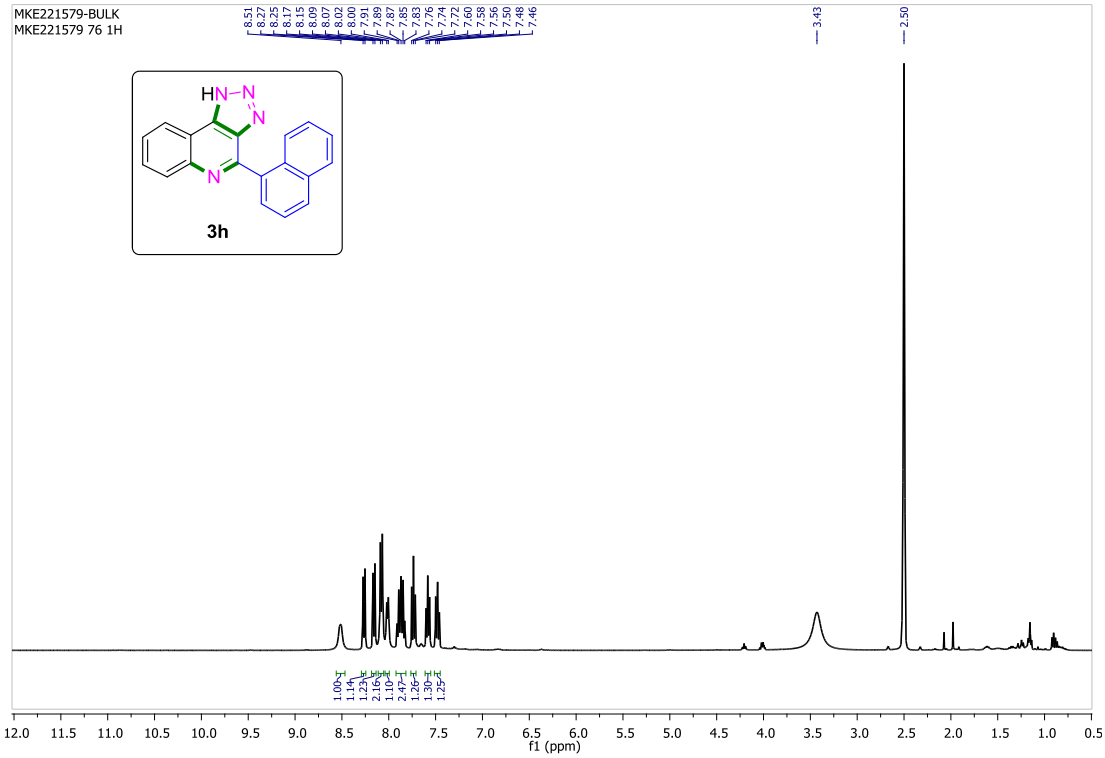


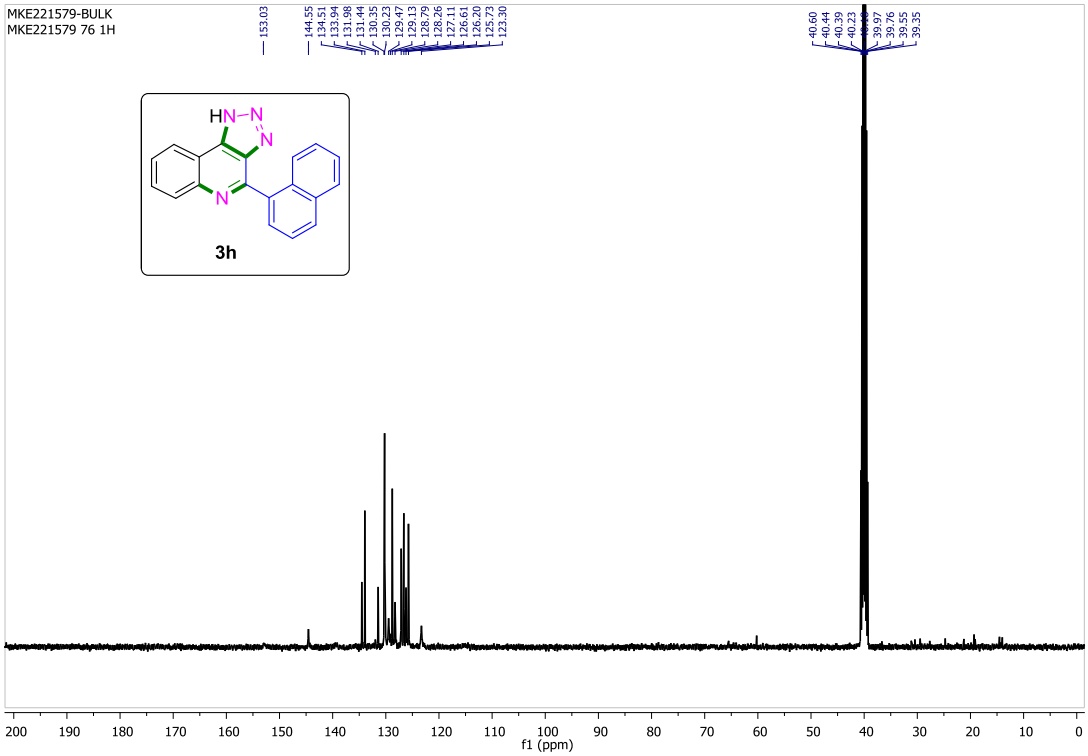
8-chloro-4-phenyl-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3g)



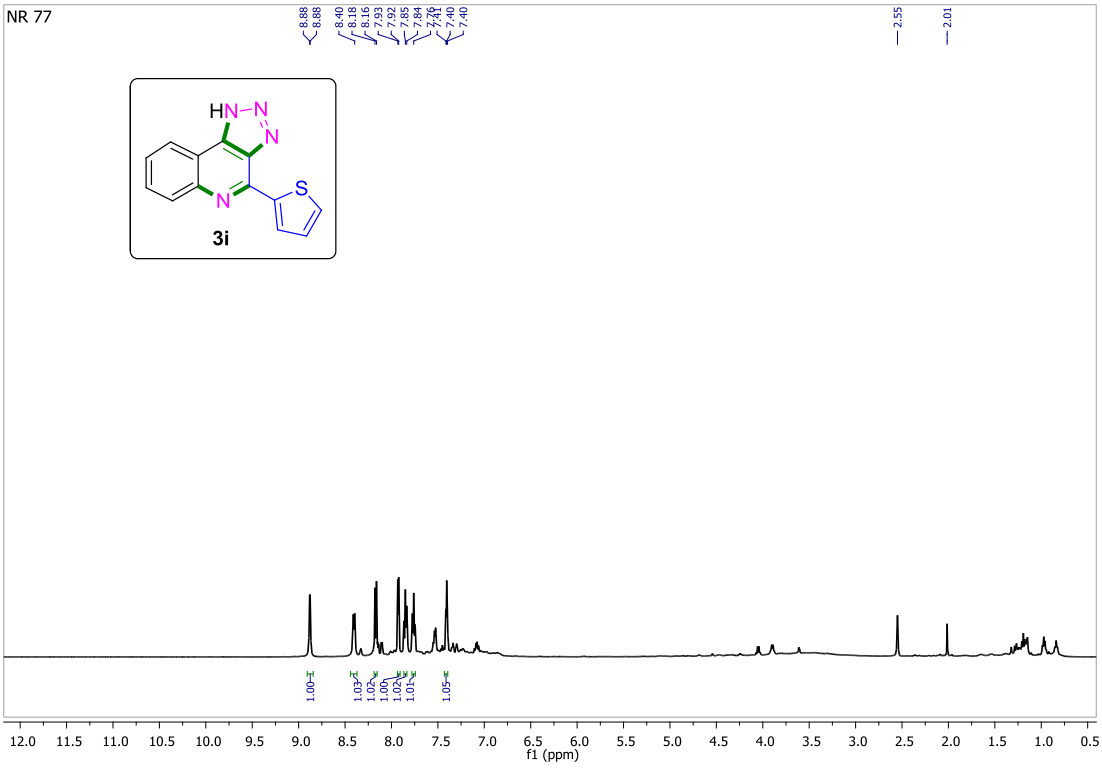


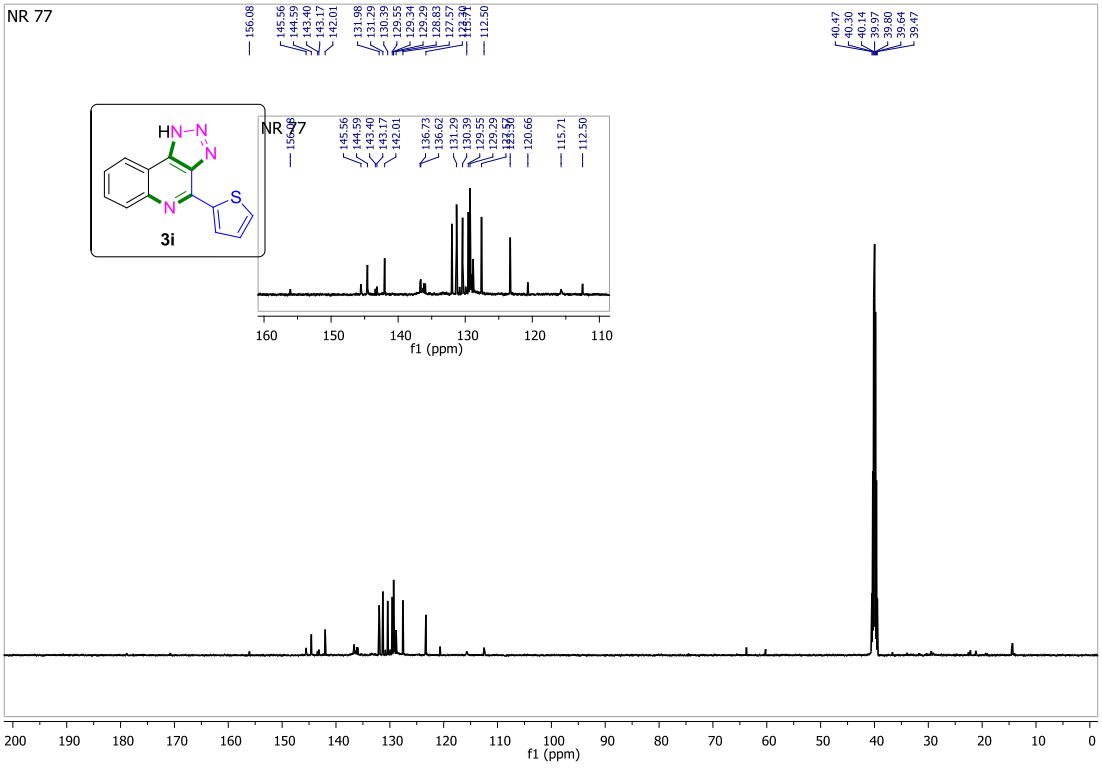
4-(naphthalen-1-yl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3h)



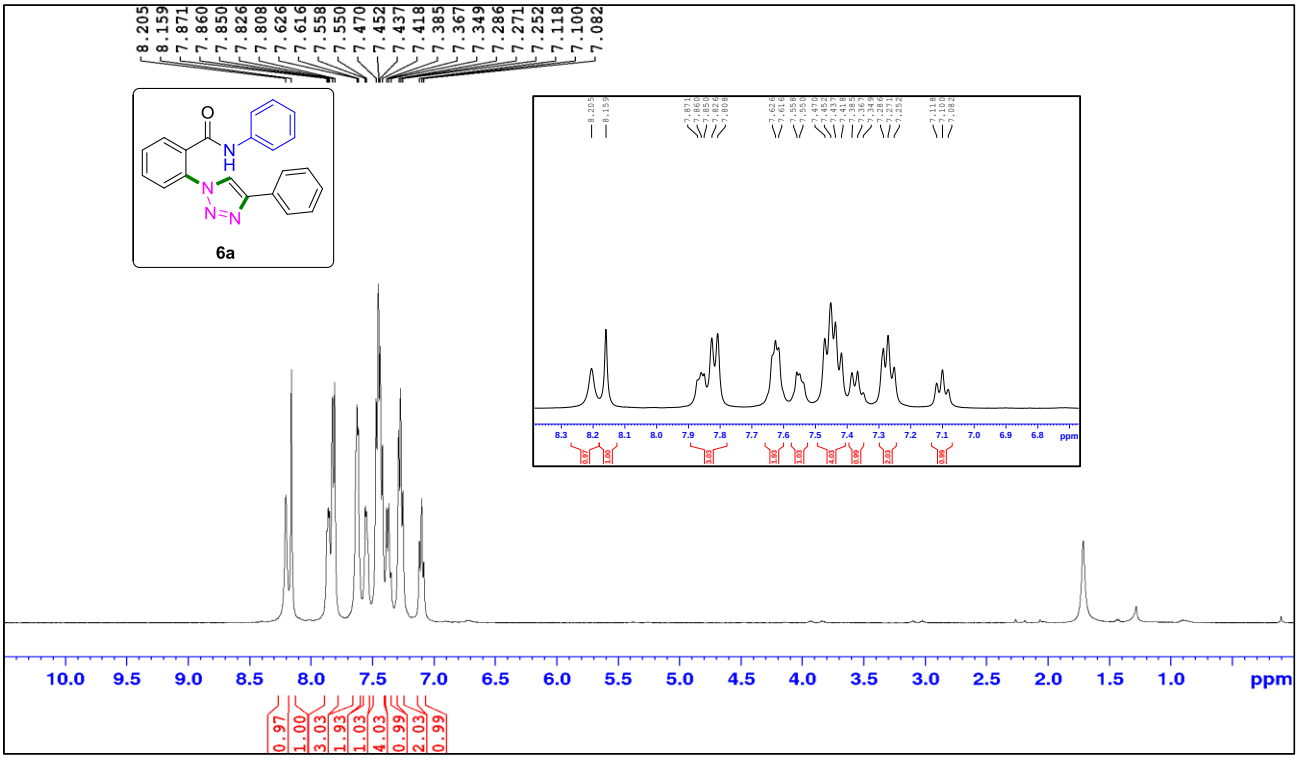


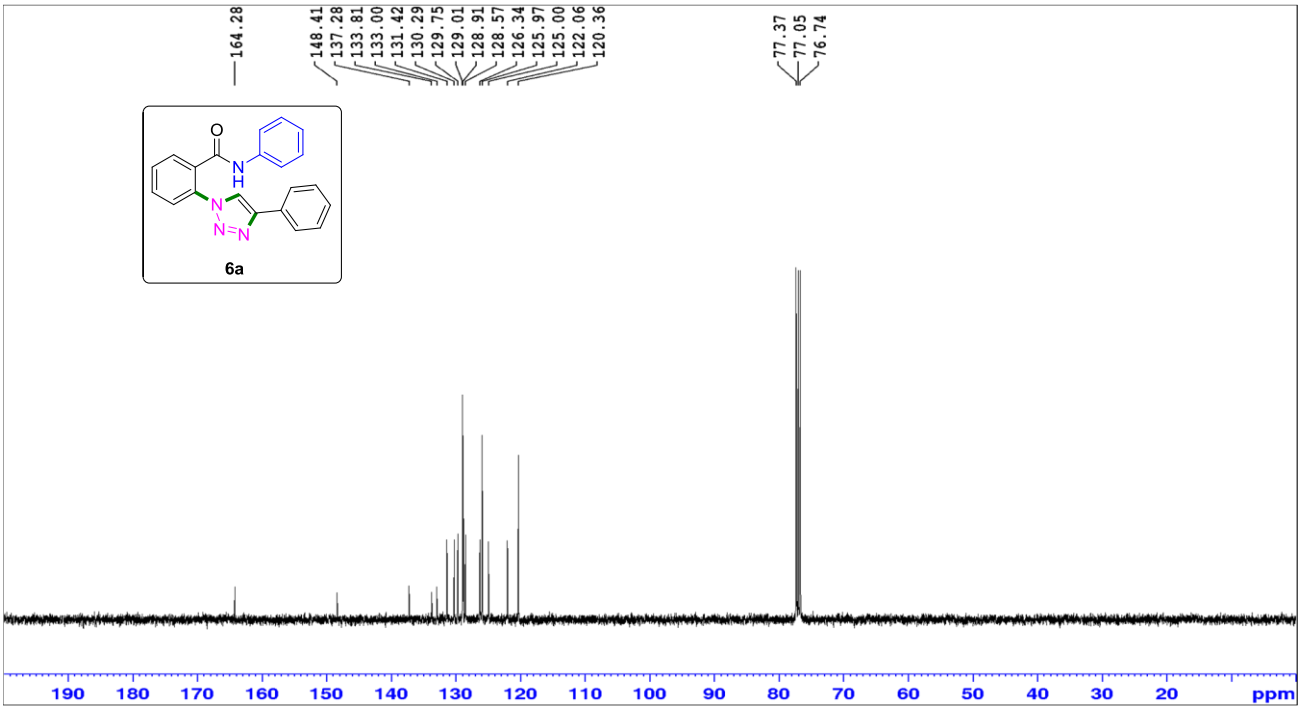
4-(thiophen-2-yl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline (3i)



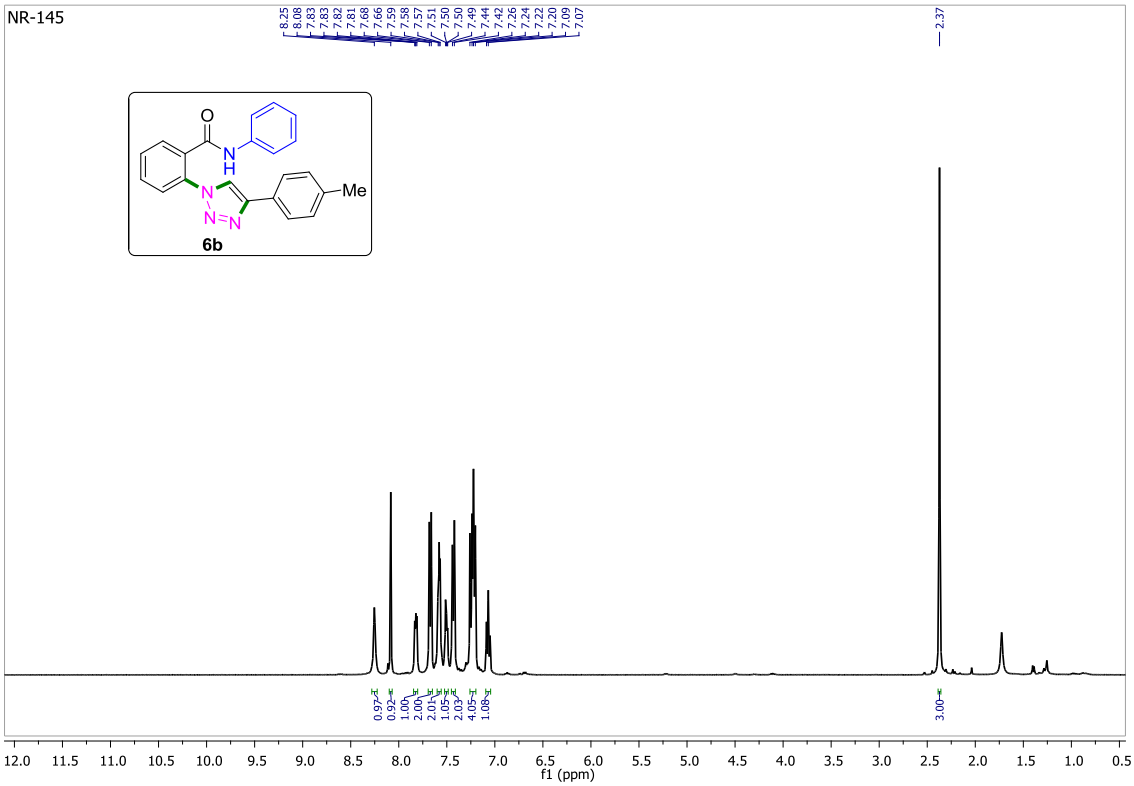


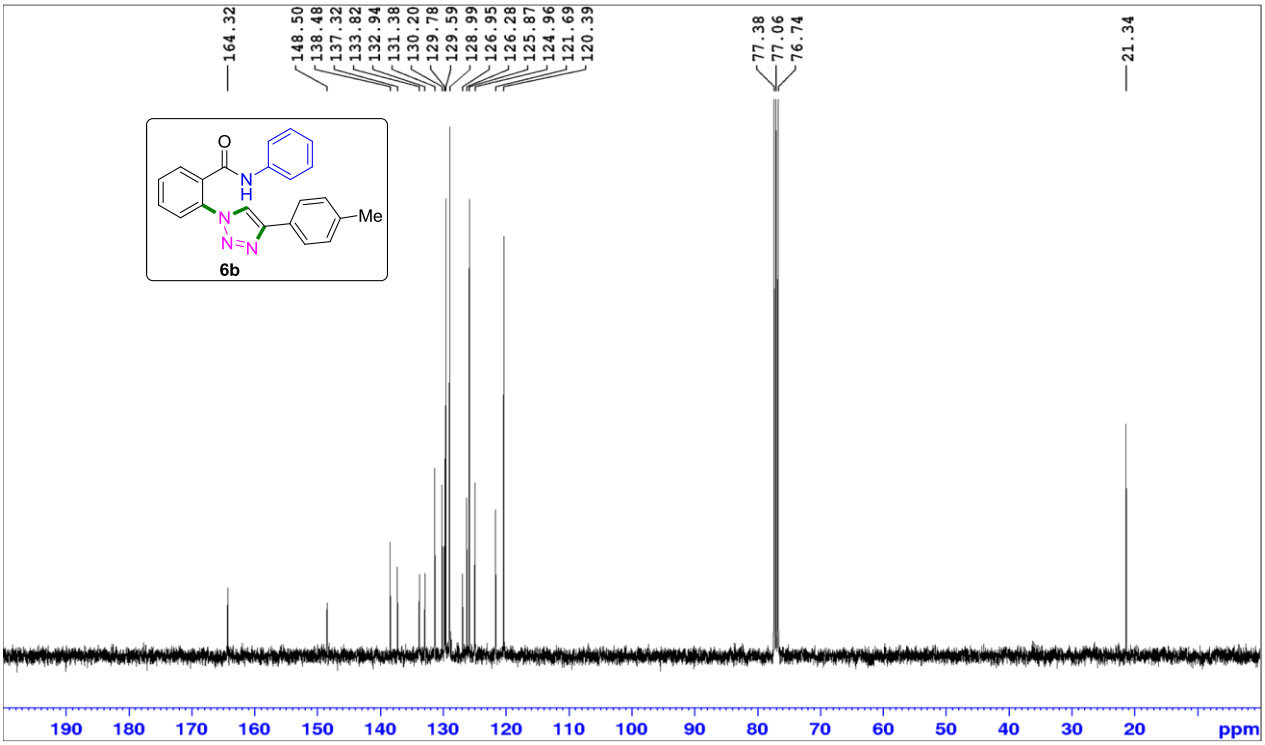
***N*-phenyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide (6a)**



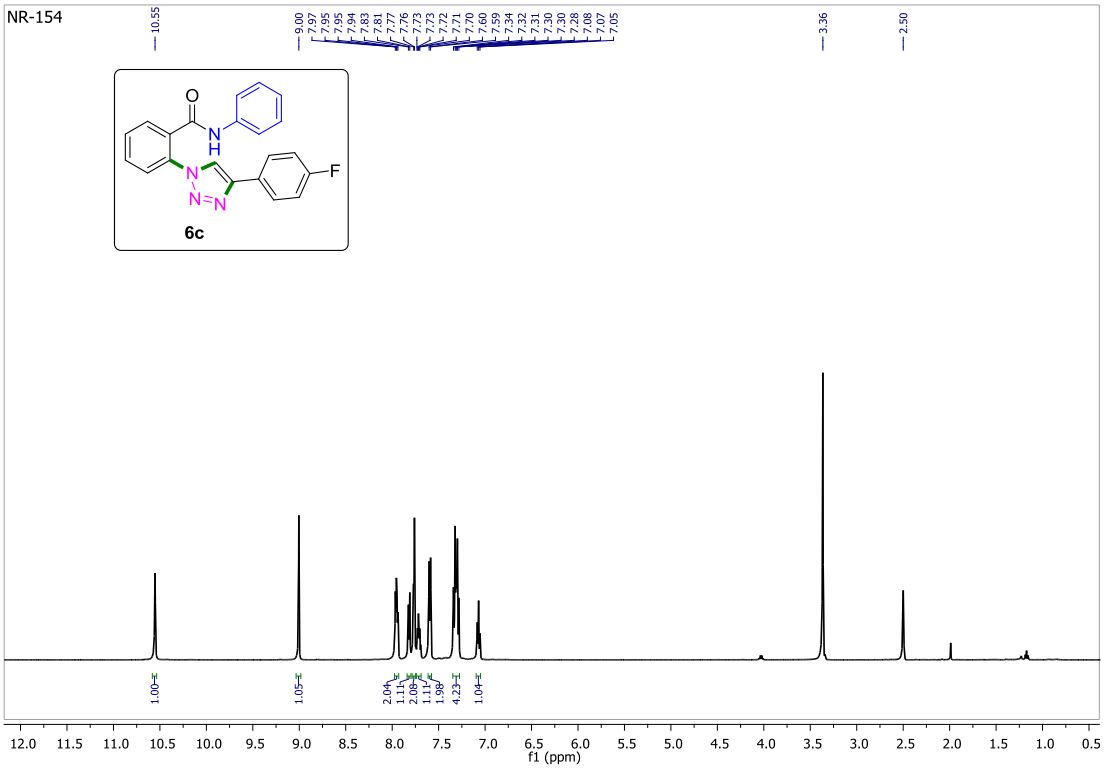


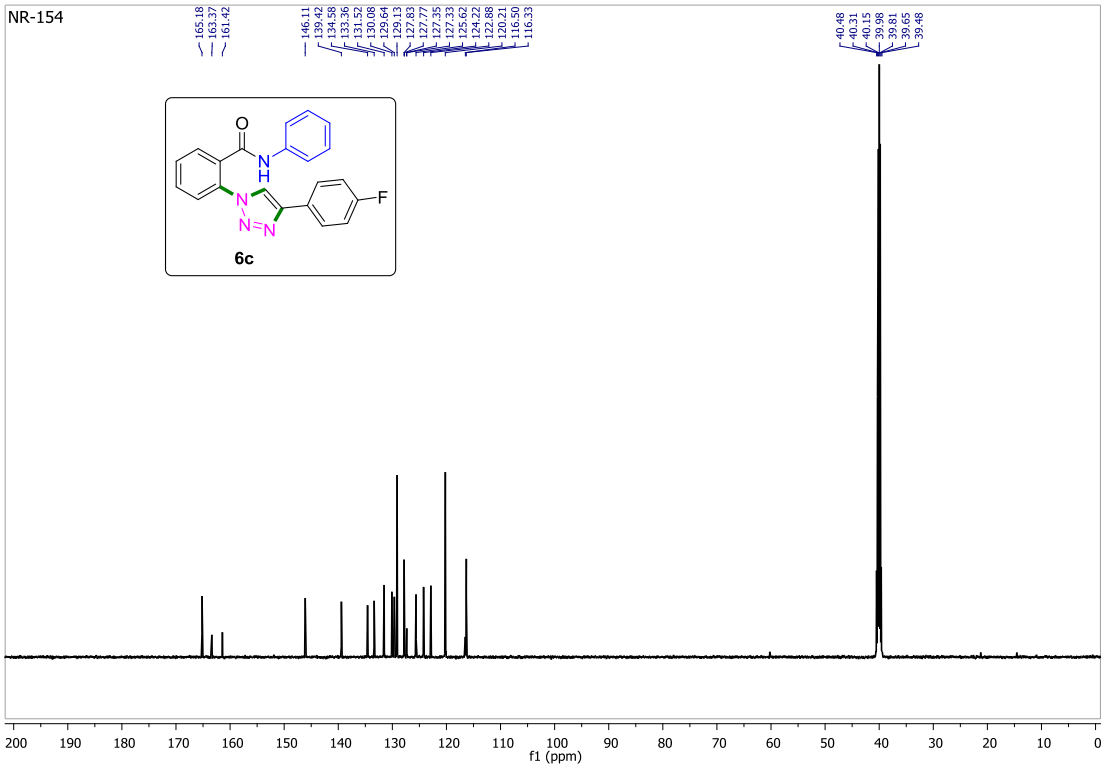
***N*-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide (6b)**



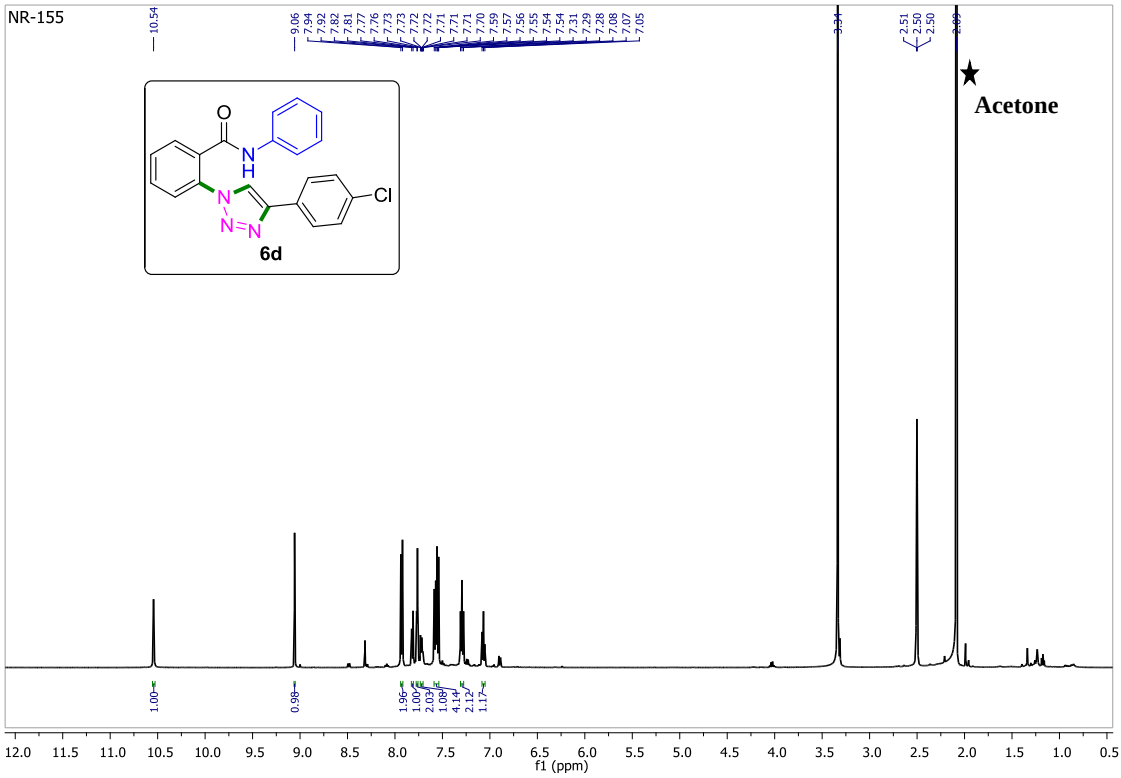


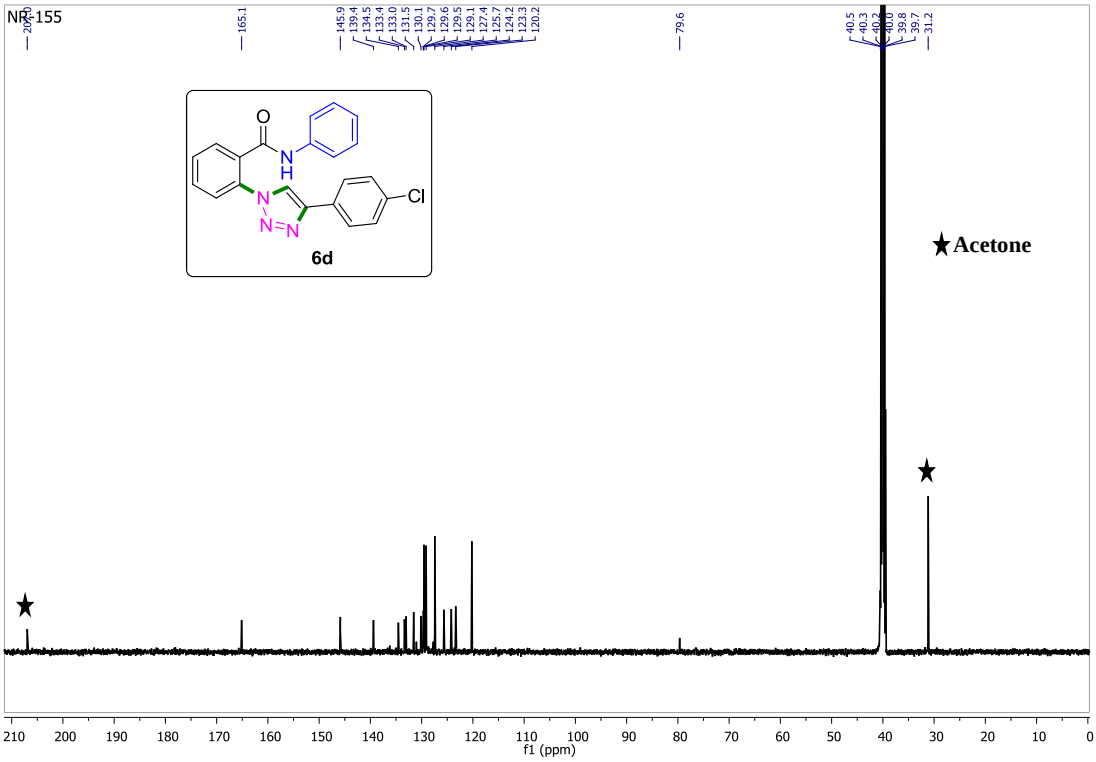
2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide (6c)



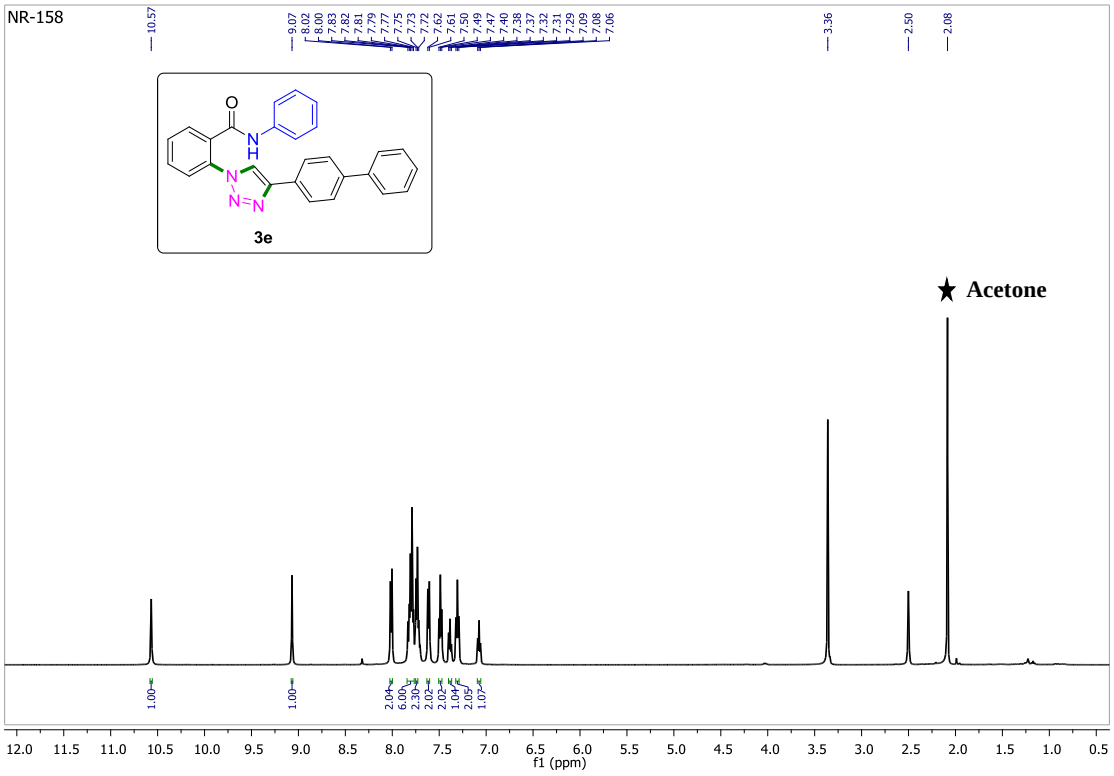


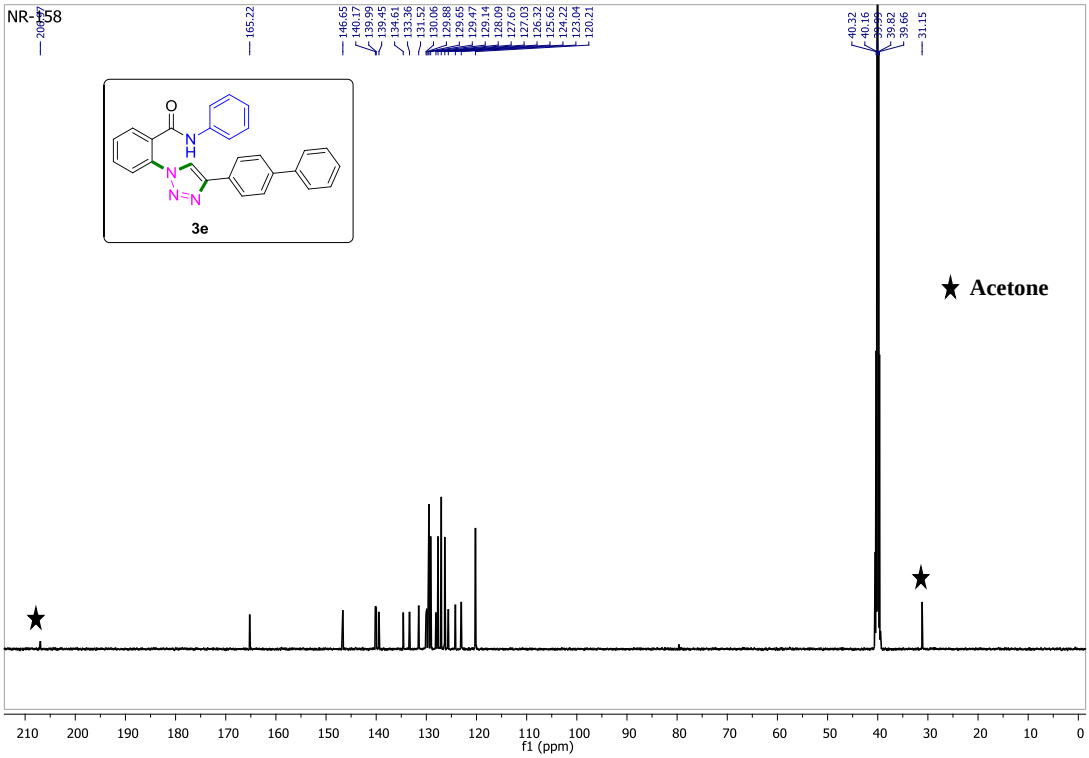
2-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide (6d)



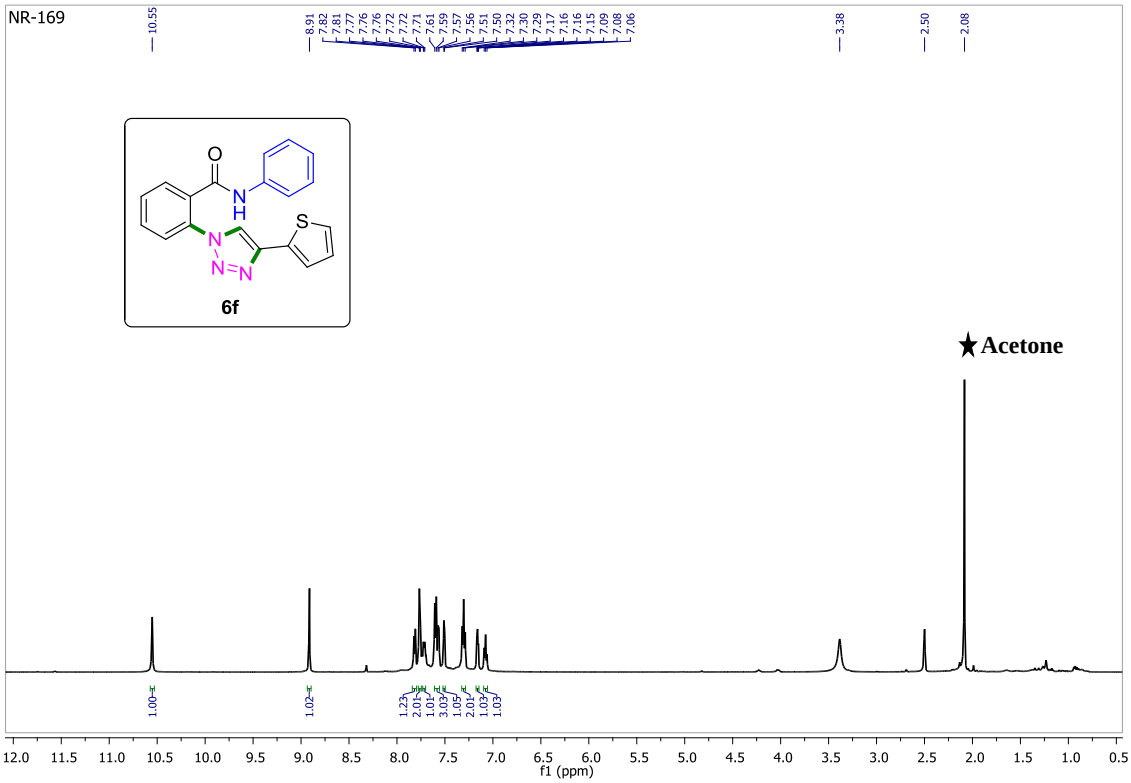


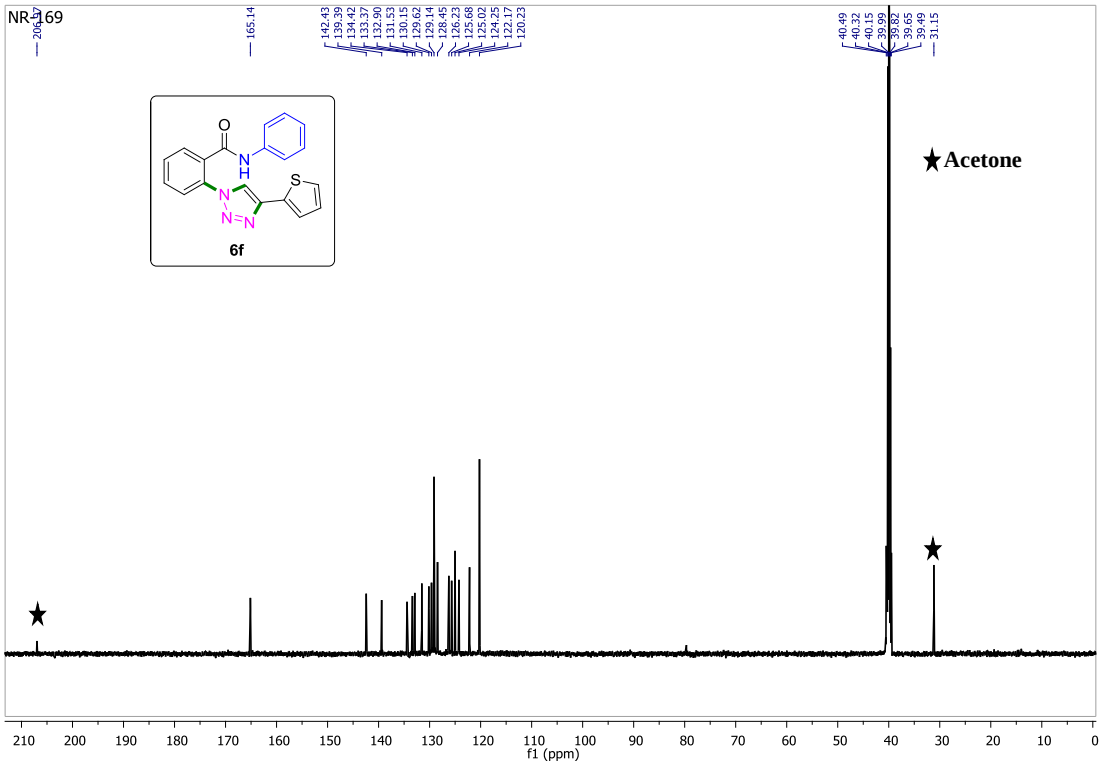
2-(4-([1,1'-biphenyl]-4-yl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide (6e)



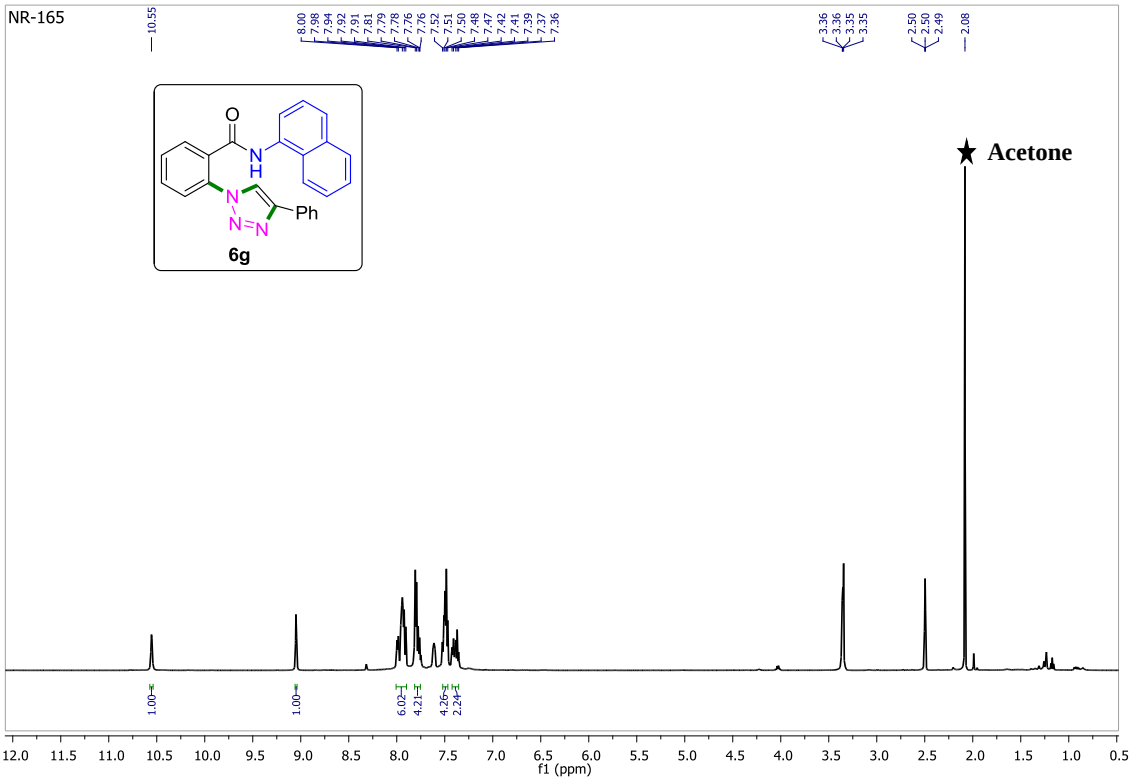


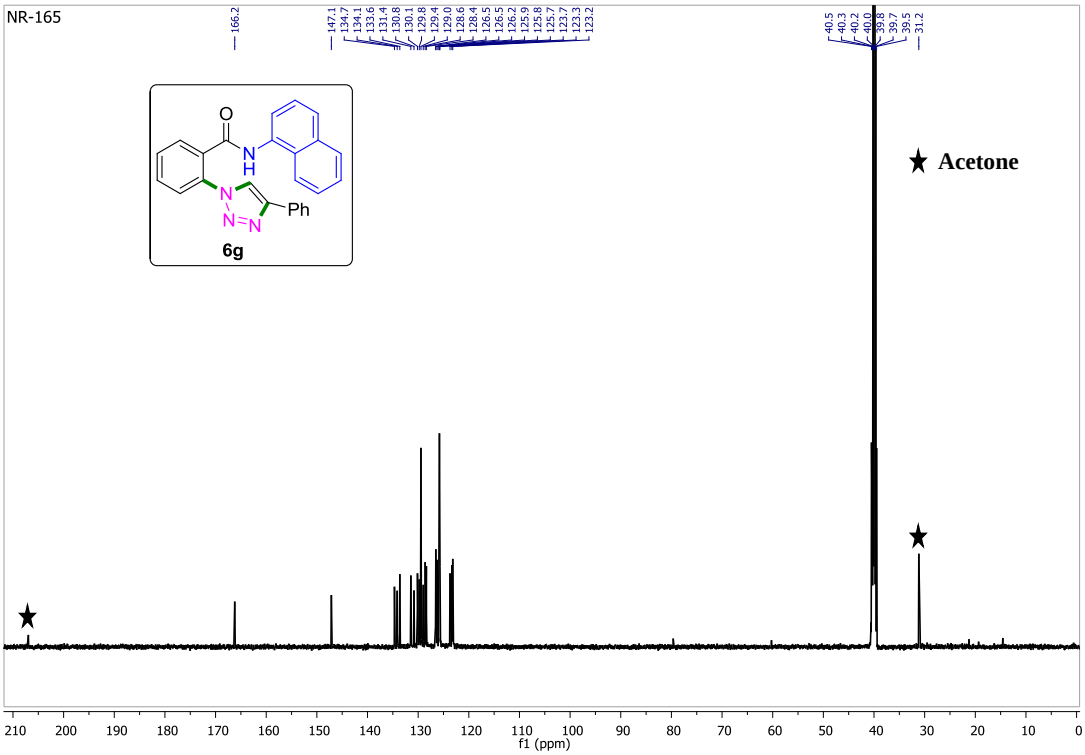
***N*-phenyl-2-(4-(thiophen-2-yl)-1*H*-1,2,3-triazol-1-yl)benzamide (6f)**



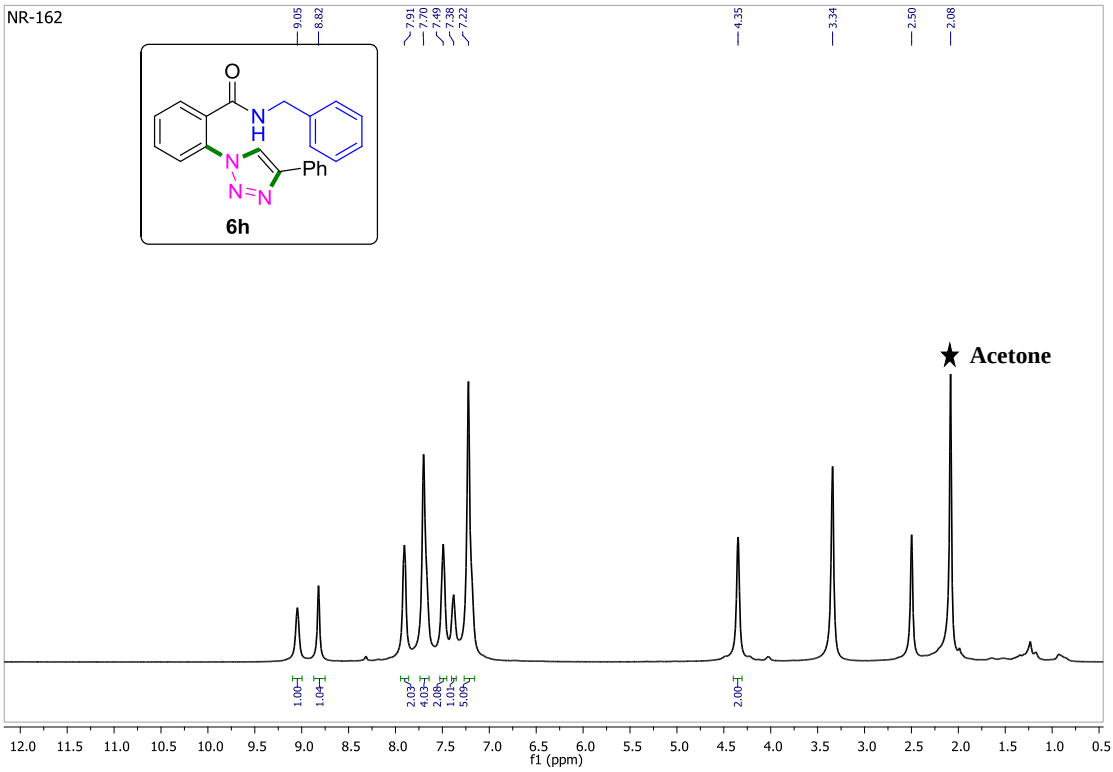


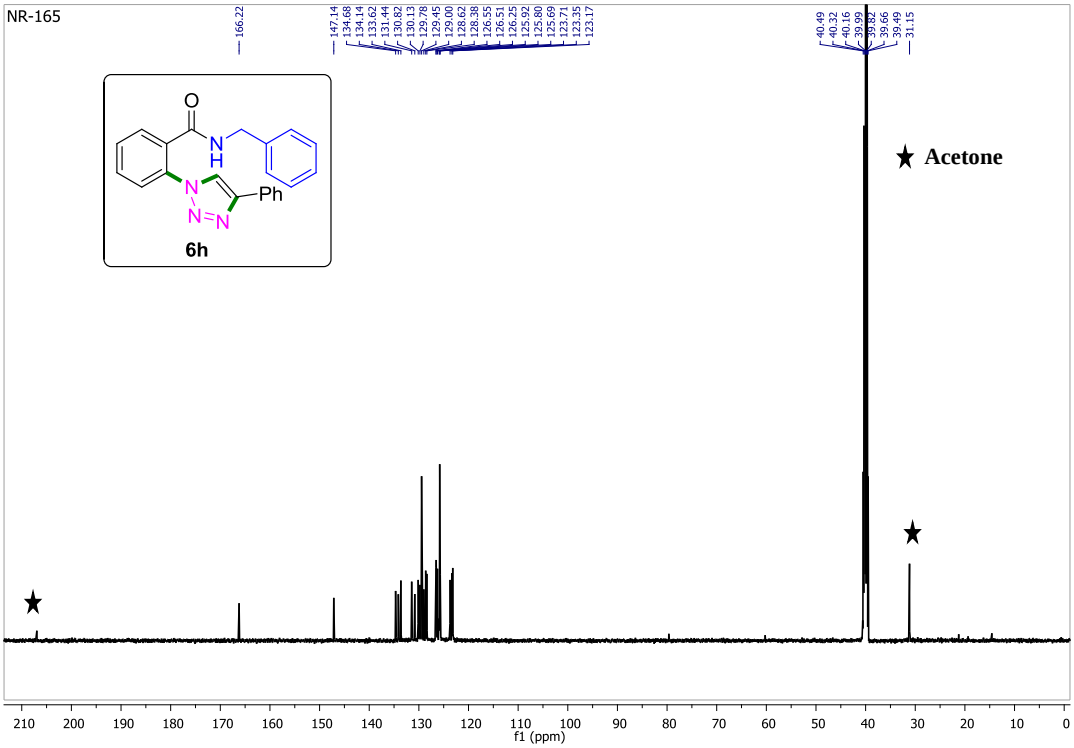
***N*-(naphthalen-1-yl)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide (6g)**



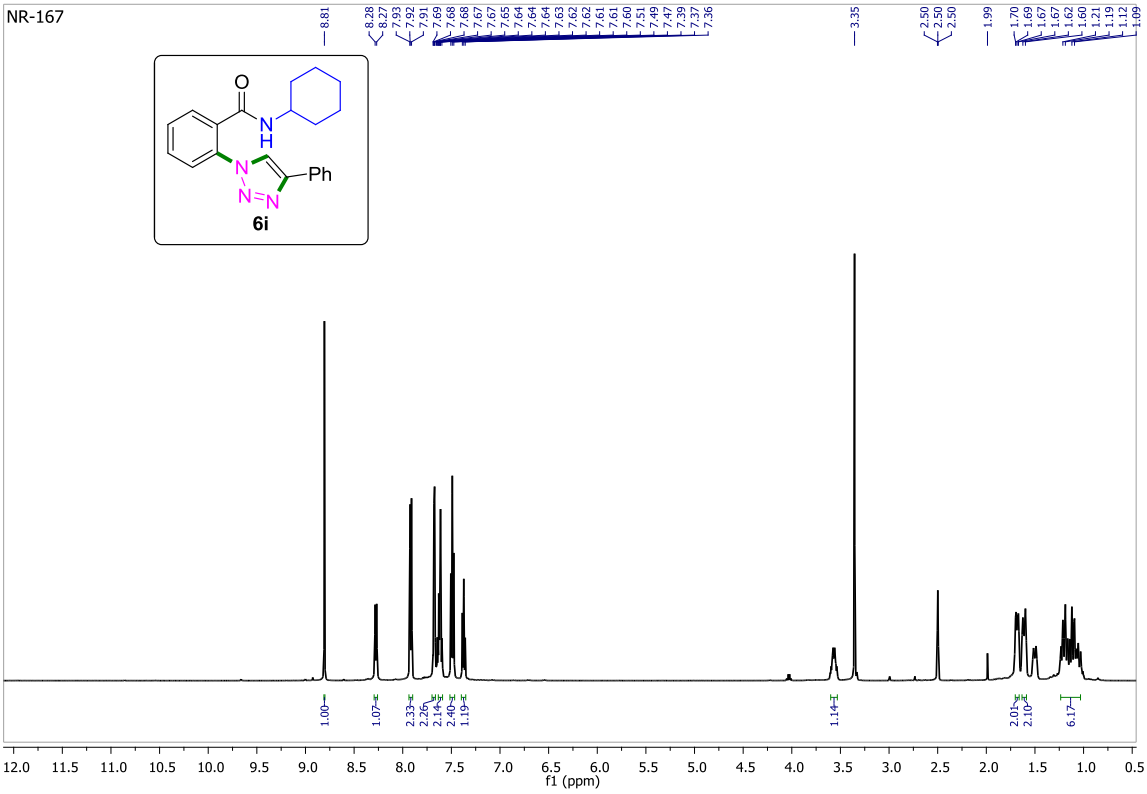


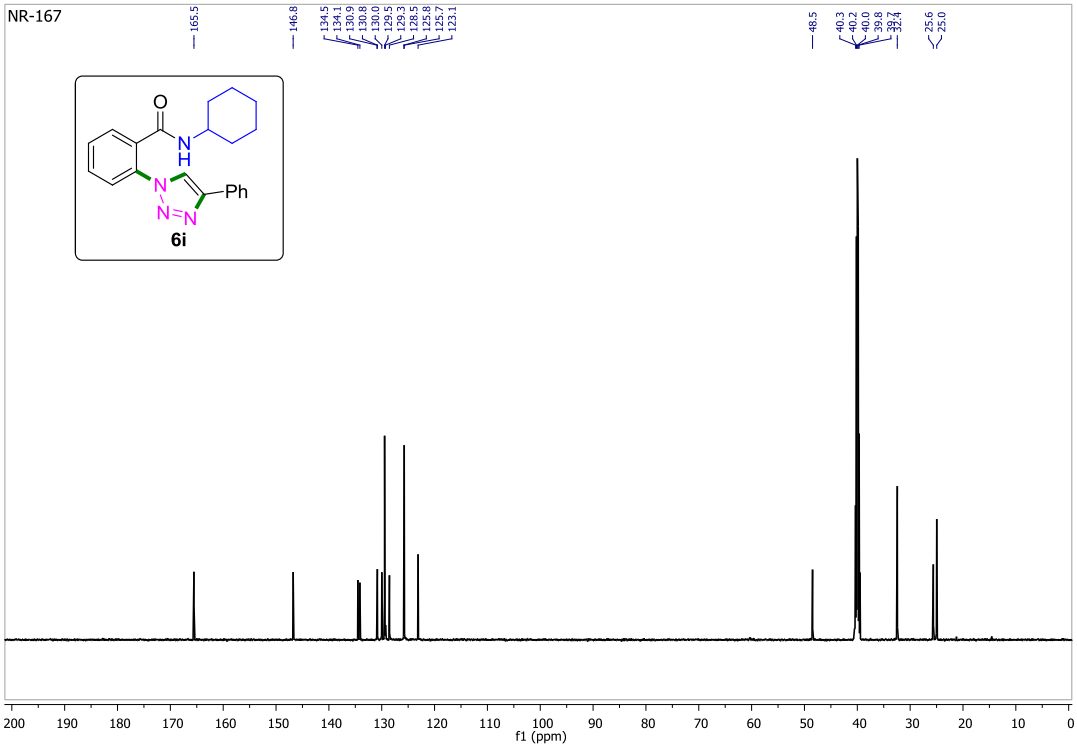
***N*-benzyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide (6h)**



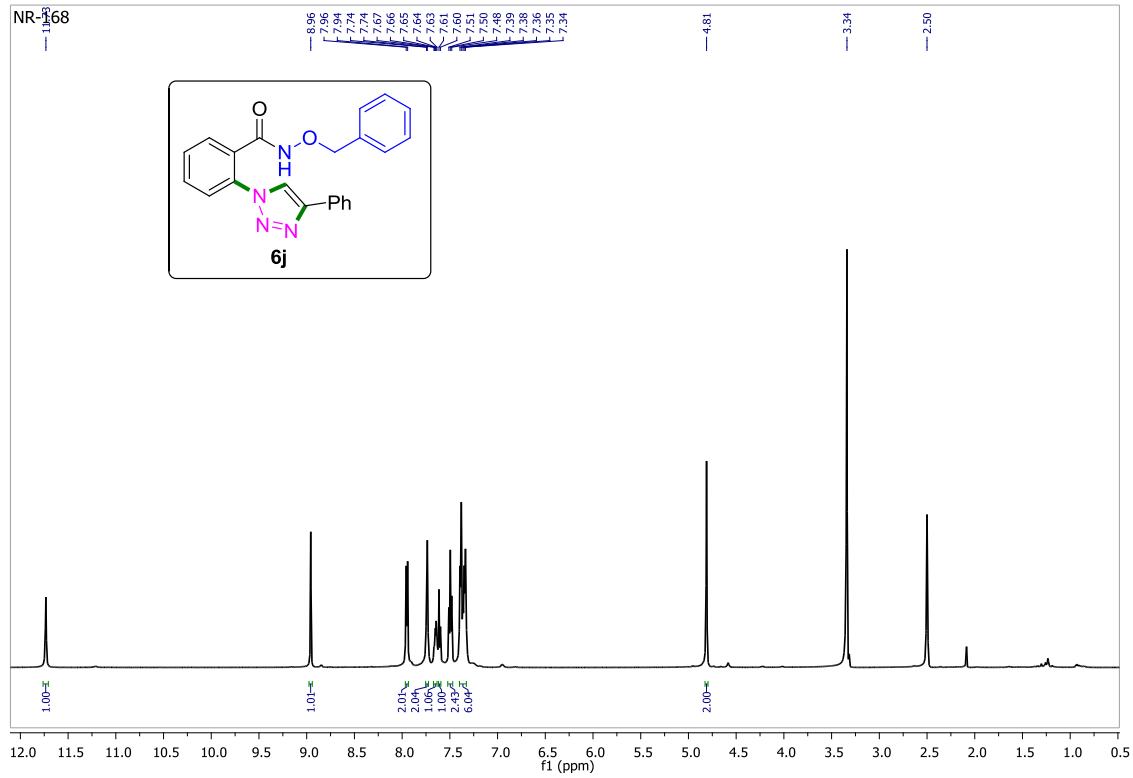


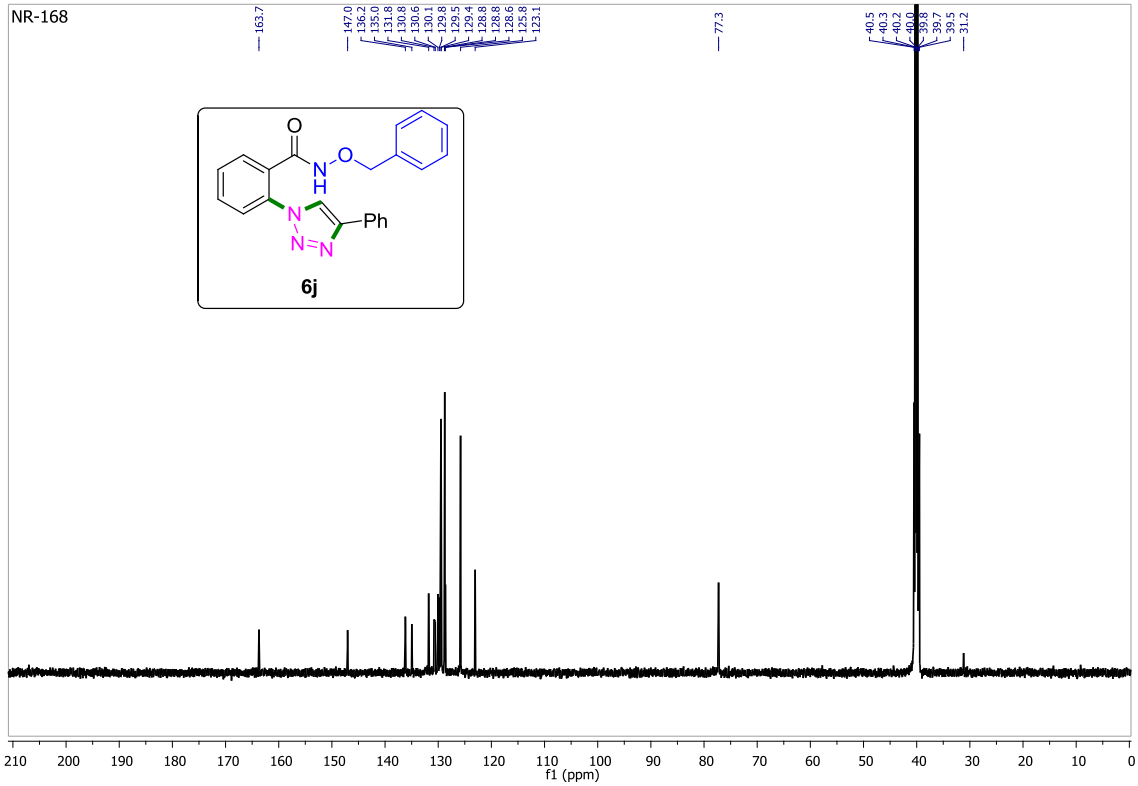
N-cyclohexyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide (6i)



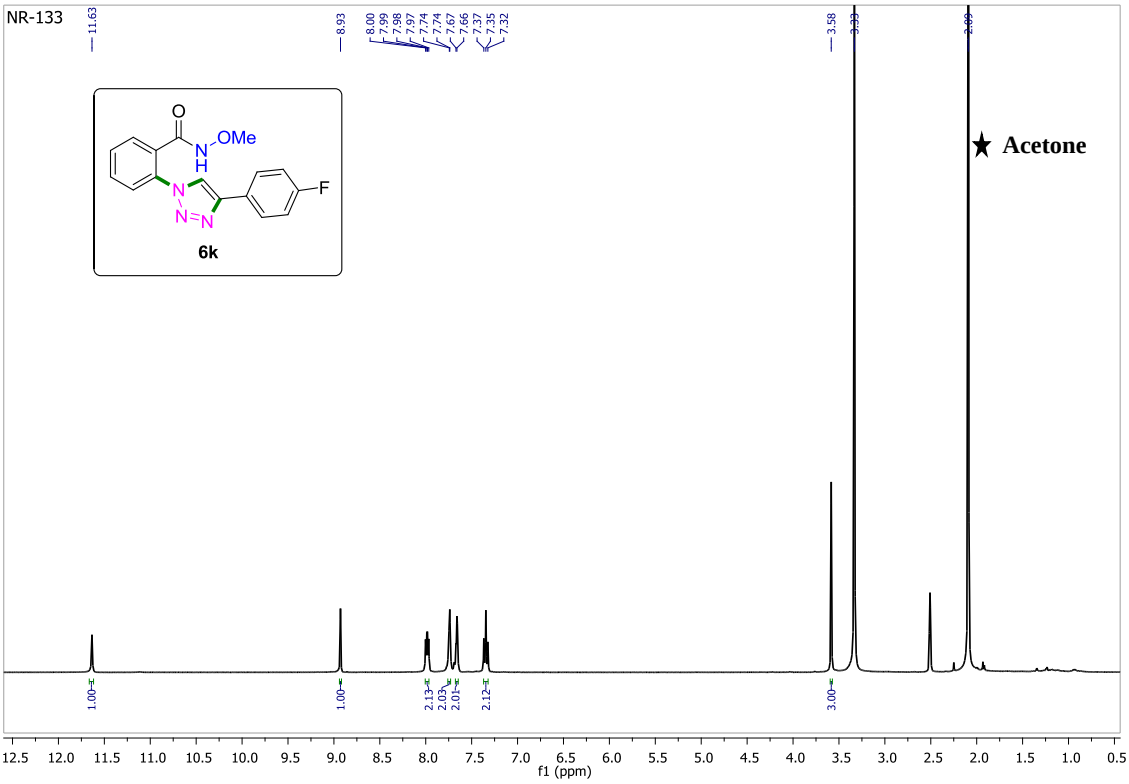


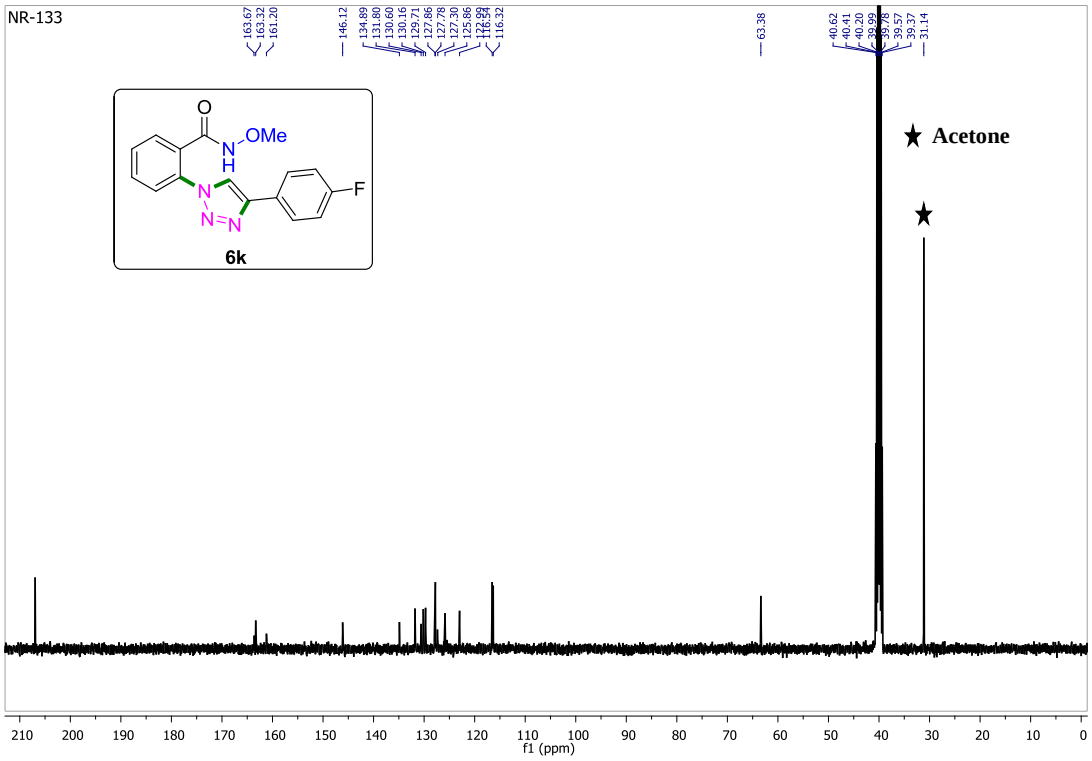
***N*-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide (6j)**



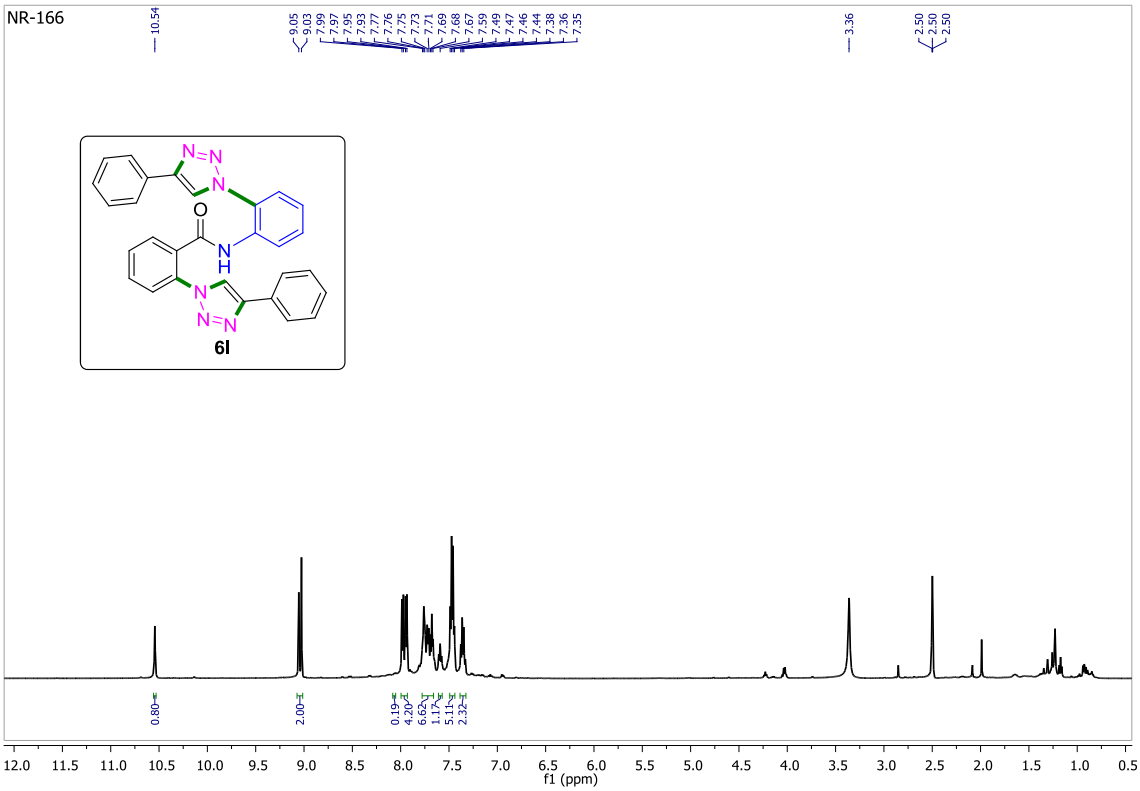


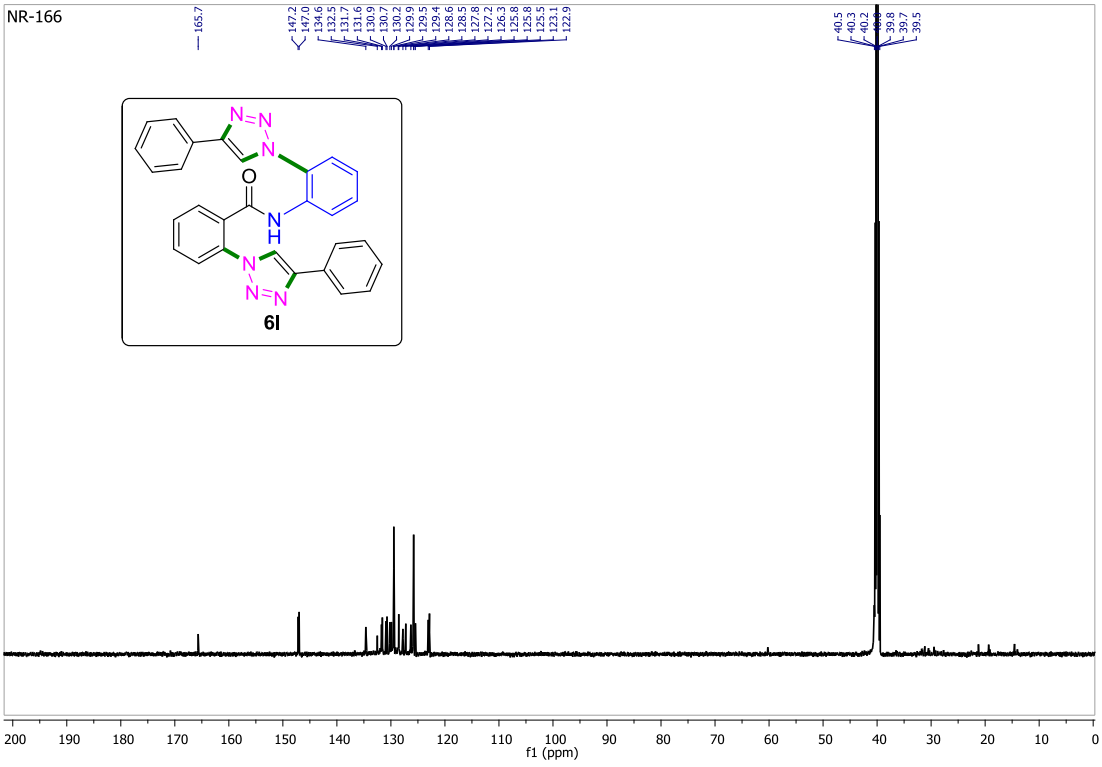
2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-methoxybenzamide (6k)





2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-*N*-(2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)phenyl)benzamide (6l)



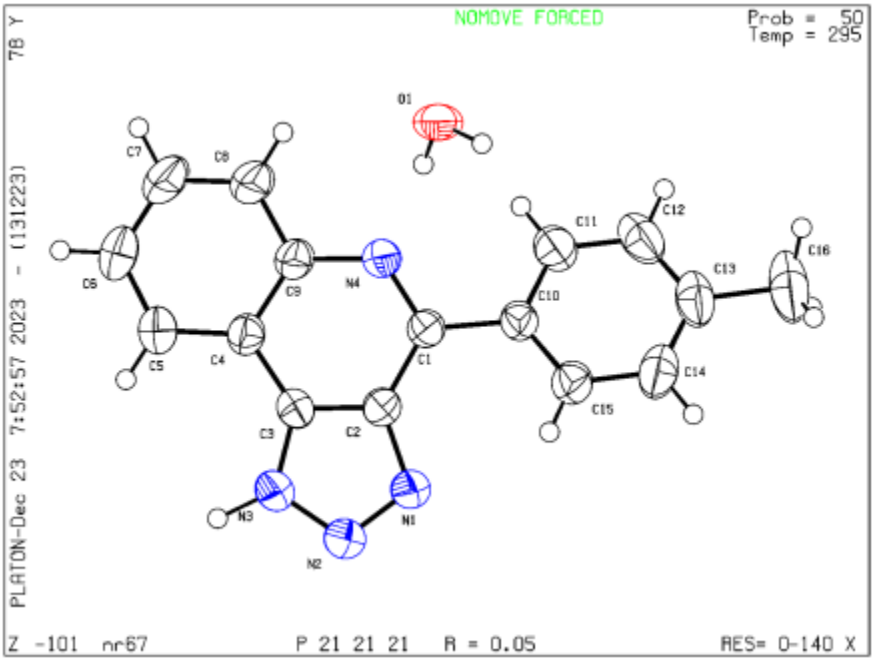


Appendix II: Crystallogaphic data

Crystallographic data of compound 3b

The crystals were mounted in turn, on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector, and used for data collection. X–ray intensity data were collected with graphite monochromated MoKα radiation (λ=0.71073 Å) at a temperature of 295(2) K, with ω scan mode. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.37.46) were applied. All the non–hydrogen atoms were refined anisotropically using full–matrix, least–squares technique. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement and refined as "riding" on the adjacent carbon atom with individual isotropic temperature factor equal 1.2 times the value of equivalent temperature factor of the parent atom. The Olex2[3] and SHELXS, SHELXL[4] programs were used for all the calculations. Four fluorine atoms of the hexafluorophosphate anion were disordered over two sets. The geometrical calculations were carried out using the PLATON program. The graphics for molecular structures, pi-pi stacking and packing images for publication were obtained using Olex2 and MERCURY software packages.

Crystal sample preparation of 3b



Crystal of **3b** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

Table S6: Crystallographic data and the structure refinement detail for 4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

Name	4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline
Formula	$C_{16}H_{12}N_4$
Formula weight	260.29
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	7.0728
b (Å)	12.2024
c (Å)	16.3422
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1410.42(17)
Z	4
Density(calcd) (g/cm^3)	1.311
Abs. coeff. (mm^{-1})	0.086
F(000)	584.0
Crystal size (mm)	0.14×0.06×0.04
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	29.506, 58.54
Data set	3540/0/203

R (int)	0.0493
N_{ref}, N_{par}	4045, 203
R, wR_2, S	0.0493, 0.1220, 1.054

Important bond lengths of 4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

Bond distances	
Module	Bond distance (Å)
N1 -N2	1.303(3)
N1-C2	1.378 (3)
N2-N3	1.347 (3)
N3-C3	1.344 (3)
N4-C9	1.384 (3)
C1-C2	1.429 (3)
C1-C10	1.480 (3)
C2-C3	1.373 (3)
C3-C4	1.410 (3)
C4-C5	1.404 (3)
C4-C9	1.416 (3)
C5-C6	1.368 (4)
C6-C7	1.384 (4)
C7-C8	1.370 (4)
C8-C9	1.387 (4)
C10-C11	1.389 (3)
C10-C15	1.381 (3)
C11-C12	1.372 (4)
C12-C13	1.377 (4)
C13-C14	1.382 (4)

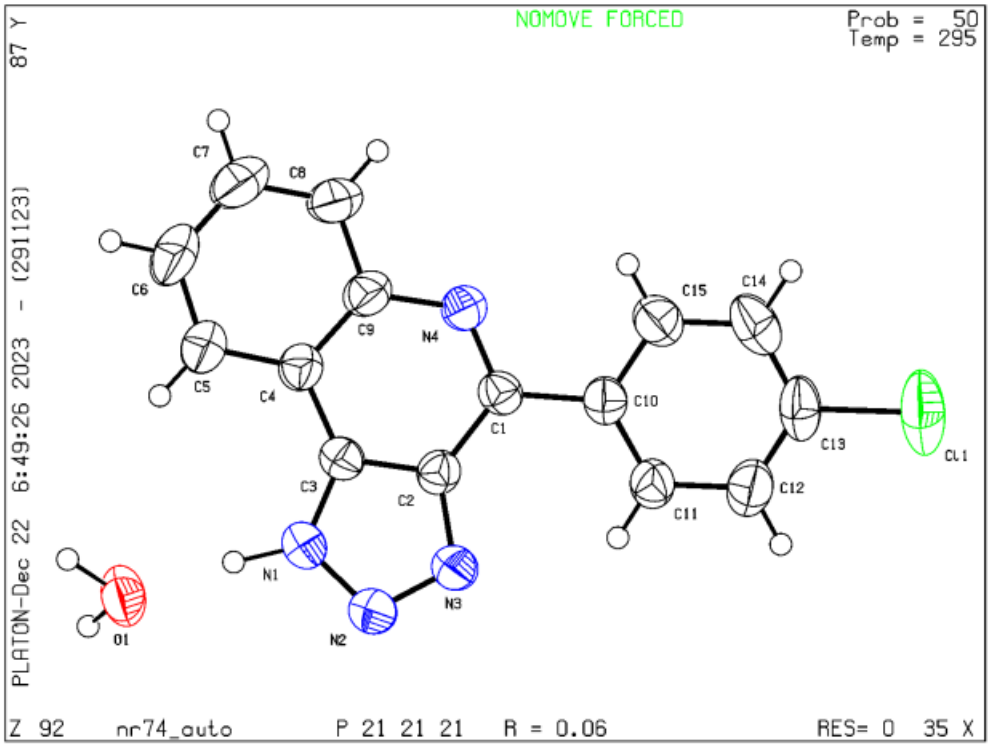
C13-C16	1.504 (4)
C14-C15	1.382 (4)

Important bond angles of 4-(p-tolyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

Module	Bond angle (^{o})
N2-N1-C2	107.75 (19)
N1-N2-N3	108.77 (19)
C3-N3-N2	110.1 (2)
C1-N4-C9	121.89 (18)
N4-C1-C2	118.3 (2)
N4-C1-C10	117.46 (18)
C2-C1-C10	124.3 (2)
N1-C2-C1	131.5 (2)
C3-C2-N1	108.21 (3)
C3-C2-C1	120.3 (2)
N3-C3-C2	105.1 (2)
N3-C3-C4	132.2 (2)
C2-C3-C4	122.64 (19)
C3-C4-C9	113.7 (2)
C5-C4-C3	126.3 (2)
C5-C4-C9	119.9 (2)
C6-C5-C4	119.7 (2)
C5-C6-C7	120.3 (3)
C8-C7-C6	120.9 (3)
C7-C8-C9	120.7 (3)
N4--C9-C4	123.2 (2)
N4-C9-C8	118.4 (2)
C8-C9-C4	118.5 (2)

C11-C10-C1	119.5 (2)
C15-C10-C1	122.3 (2)
C15-C10-C11	118.2 (2)
C12-C11-C10	120.5 (3)
C11-C12-C13	122.1 (3)
C12-C13-C14	117.1 (2)
C12-C13-C16	121.3 (3)
C14-C13-C16	121.7 (3)
C16-C17-C22	121.8 (3)
C10-C15-C14	120.3 (2)

Crystal sample preparation of 3d



Crystal of **3d** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

Table S7: Crystallographic data and the structure refinement detail for 4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

Name	4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline
Formula	$C_{15}H_9ClN_4$
Formula weight	280.71
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	7.0038
b (Å)	12.3433
c (Å)	16.3586
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1414.2(3)
Z	4
Density(calcd) (g/cm^3)	1.403
Abs. coeff. (mm^{-1})	0.274
F(000)	616.0
Crystal size (mm)	0.17×0.05×0.05
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	7.056, 58.738
Data set	3557/0/202
R (int)	0.0634
N_{ref}, N_{par}	3905, 202
R, wR_2, S	0.0552, 0.1150, 0.995

Important bond lengths of 4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

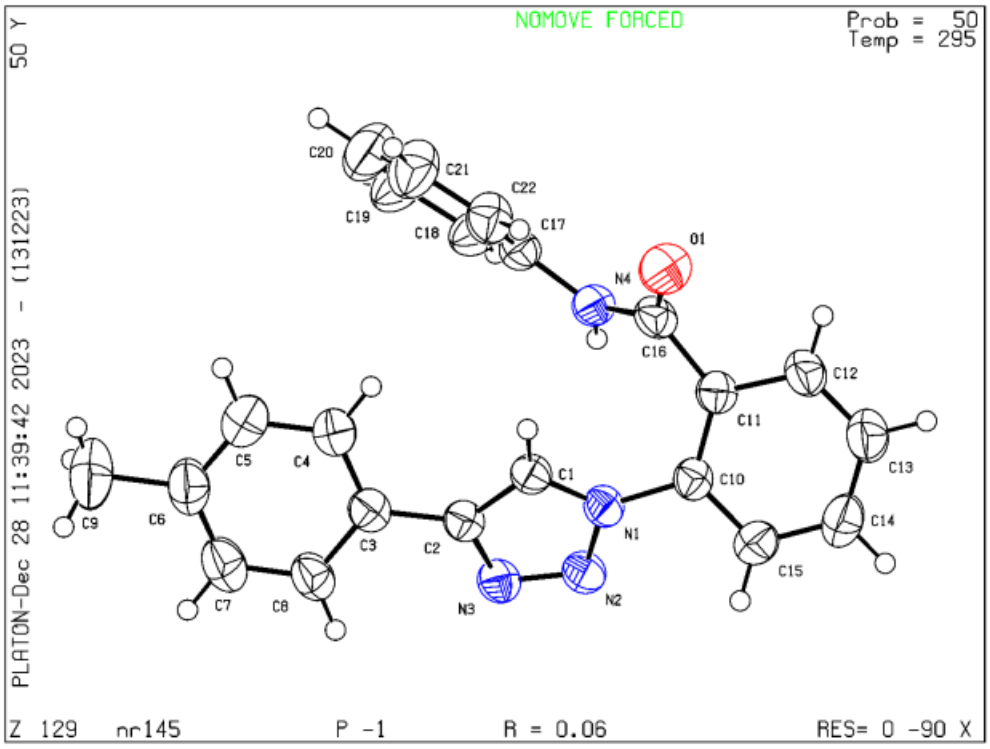
Bond distances	
Module	Bond distance (Å)
C11-C13	1.742 (4)
N1-N2	1.349 (4)
N1-C3	1.345 (4)
N2-N3	1.318 (5)
N3-C2	1.376 (4)
N4-C1	1.311 (4)
N4-C9	1.386 (4)
C1-C2	1.424 (4)
C1-C10	1.494 (4)
C2-C3	1.389 (4)
C3-C4	1.419 (5)
C4-C5	1.406 (5)
C4-C9	1.412(5)
C5-C6	1.371(5)
C6-C7	1.381(7)
C7-C8	1.377(6)
C8-C9	1.397(5)
C10-C11	1.381(5)
C10-C15	1.396(5)
C11-C12	1.386(5)
C12-C13	1.366(5)
C14-C15	1.376(5)

Important bond angles of 4-(4-chlorophenyl)-1*H*-[1,2,3]triazolo[4,5-c]quinoline

Module	Bond angle (°)
C3-N1-N2	110.6(3)
N3-N2-N1	108.1(3)
N2-N3-N1	108.4(3)
C1-N4-C9	121.8(3)
N4-C1-C2	119.0(3)
N4-C1-C10	117.4(3)
C2-C1-C10	123.6(3)
N3-C2-C1	132.6(3)
C3-C2-C1	107.6(3)
N1-C3-C2	119.7(3)
N1-C3-C4	105.2(3)
C2-C3-C4	132.3(3)
C5-C4-C9	122.4(3)
C9-C4-C3	126.0(3)
C6-C5-C4	120.4(3)
C6-C5-C4	113.6(3)
C5-C6-C7	119.3(4)
C8-C7-C6	120.5(4)
C8-C7-C6	121.2(4)
C7-C8-C9	120.0(4)
N4--C9-C4	123.5(3)
N4-C9-C8	118.0(3)
C8-C9-C4	118.5(3)
C11-C10-C1	122.4(3)
C11-C10-C15	118.7(3)
C15-C10-C1	118.9(3)
C10-C11-C12	120.9(4)

C13-C12-C11	119.4(4)
C12-C13-C11	119.5(4)
C12-C13-C14	121.1(4)
C14-C13-C16	119.4(3)
C16-C17-C11	119.5(4)
C14-C15-C10	120.4(4)

Crystal sample preparation of 6b



Crystal of **6b** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

Table S8: Crystallographic data and the structure refinement detail for *N*-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide

Name	*N*-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide
Formula	$C_{22}H_{18}N_4O$
Formula weight	354.41
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	7.5949(8)
b (Å)	9.8677(12)
c (Å)	12.6331(15)
α (°)	80.581(10)
β (°)	89.926(9)
γ (°)	73.743(10)
V (Å^3)	895.68(18)
Z	2
Density(calcd) (g/cm^3)	1.314
Abs. coeff. (mm^{-1})	0.084
F(000)	372.0
Crystal size (mm)	0.11×0.08×0.04
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	6.612, 59.14
Data set	4233/0/249
R (int)	0.1362
N_{ref}, N_{par}	4233, 249
R, wR_2, S	0.0566, 0.0922, 0.898

Important bond lengths of *N*-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide

Bond distances	
Module	Bond distance (Å)
O1-C16	1.219(3)
N1-N2	1.352(3)
N1-C1	1.343(3)
N1-C10	1.433(3)
N2-N3	1.309(3)
N3-C2	1.362(3)
N4-C16	1.354(3)
N4-C17	1.409(3)
C1-C2	1.363(3)
C2-C3	1.463(3)
C3-C4	1.368(4)
C3-C8	1.389(3)
C4-C5	1.383(4)
C5-C6	1.372(4)
C6-C7	1.372(4)
C6-C9	1.506(4)
C7-C8	1.371(4)
C10-C11	1.390(3)
C10-C15	1.383(3)
C11-C12	1.396(3)
C11-C16	1.494(4)
C12-C13	1.360(4)
C13-C14	1.371(4)
C14-C15	1.368(3)
C17-C18	1.388(4)
C17-C22	1.369(4)

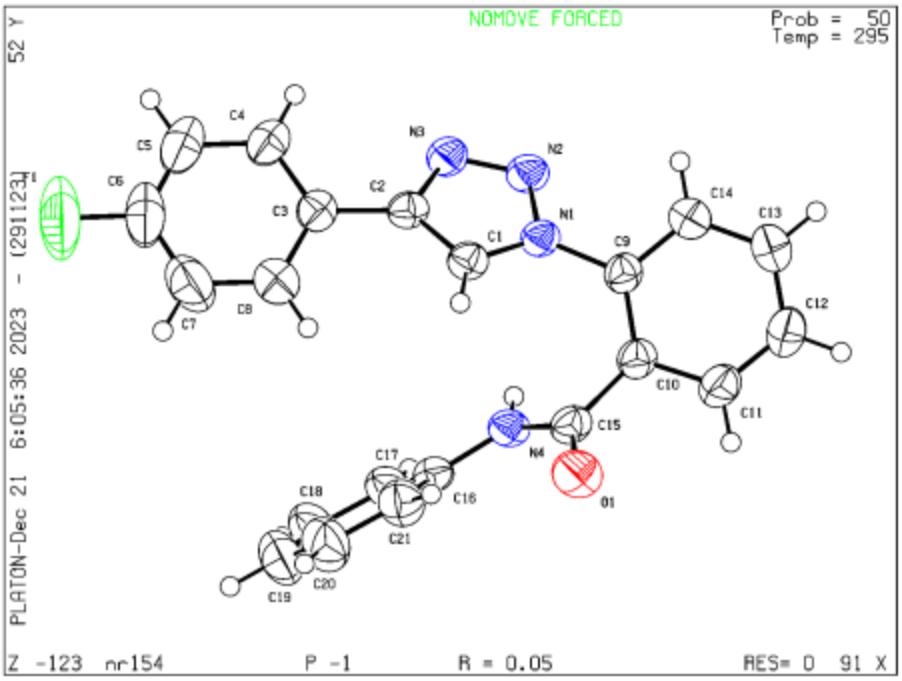
C18-C19	1.370(4)
C19-C20	1.357(5)
C20-C21	1.379(5)
C21-C22	1.382(4)

Important bond angles of *N*-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)benzamide

Module	Bond angle (^{o})
N2-N1-C10	117.5(2)
C1-N1-N2	110.6(2)
C1-N1-C10	131.7(2)
N3-N2-N1	106.6(2)
N3-N2-C2	109.6(2)
C16-N4-C17	126.4(3)
N1-C1-C2	105.5(2)
N3-C2-C1	107.6(2)
N3-C2-C3	121.4(2)
C1-C2-C3	130.8(3)
C4-C3-C2	120.8(2)
C4-C3-C8	118.3(2)
C8-C3-C2	120.7(3)
C3-C4-C5	120.4(3)
C6-C5-C4	121.5(3)
C5-C6-C9	121.7(3)
C7-C6-C5	117.9(3)
C7-C6-C9	120.4(3)
C8-C7-C6	121.3(3)
C7-C8-C3	120.6(3)
C11-C10-N1	122.0(2)

C15-C10-N1	117.3(2)
C15-C10-C11	120.6(2)
C10-C11-C12	117.5(2)
C10-C11-C16	126.3(2)
C12-C11-C16	116.1(2)
C13-C12-C11	121.7(3)
C12-C13-C14	119.6(3)
C15-C14-C13	120.6(3)
C14-C15-C10	119.8(3)
O1-C16-N4	123.5(3)
O1-C16-C11	120.0(2)
N4-C16-C11	116.5(3)
C18-C17-N4	117.4(3)
C22-C17-N4	123.4(3)
C22-C17-C18	119.1(3)
C19-C18-C17	119.8(3)
C20-C19-C18	121.2(3)
C19-C20-C21	119.4(3)
C20-C21-C22	119.9(4)
C17-C22-C21	120.5(3)

Crystal sample preparation of 6d



Crystal of **6d** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

Table S9: Crystallographic data and the structure refinement detail for 2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide

Name	2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide
Formula	$C_{21}H_{15}FN_4O$
Formula weight	358.37
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	7.6099(9)
b (Å)	9.9948(13)
c (Å)	12.3384(12)

α (°)	101.580(10)
β (°)	91.165(9)
γ (°)	107.833(11)
V (Å^3)	871.81(18)
Z	2
Density(calcd) (g/cm^3)	1.365
Abs. coeff. (mm^{-1})	0.095
F(000)	372.0
Crystal size (mm)	0.17 × 0.1 × 0.06
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	6.832, 59.014
Data set	4170/0/248
R (int)	0.1362
N_{ref}, N_{par}	4170, 248
R, wR_2, S	0.0488, 0.1154, 1.011

Important bond lengths of 2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide

Bond distances	
Module	Bond distance (Å)
F1-C6	1.361(2)
O1-C15	1.2212(18)
N1-N2	1.3530(16)
N1-C1	1.3435(19)
N1-C9	1.4343(19)
N2-N3	1.3050(18)
N3C2	1.362(2)
N4-C15	1.3491(19)

N4-C16	1.412(2)
C1-C2	1.362(2)
C2-C3	1.461(2)
C3-C4	1.388(2)
C3-C8	1.381(3)
C4-C5	1.373(3)
C5-C6	1.346(3)
C6-C7	1.368(3)
C7-C8	1.379(3)
C9-C10	1.395(2)
C9-C14	1.381(2)
C10-C11	1.391(2)
C10-C15	1.499(2)
C11-C12	1.369(3)
C12-C13	1.374(3)
C13-C14	1.380(2)
C16-C17	1.388(2)
C16-C21	1.380(2)
C17-C18	1.370(3)
C18-C19	1.372(3)
C19-C20	1.370(3)
C20-C21	1.377(3)

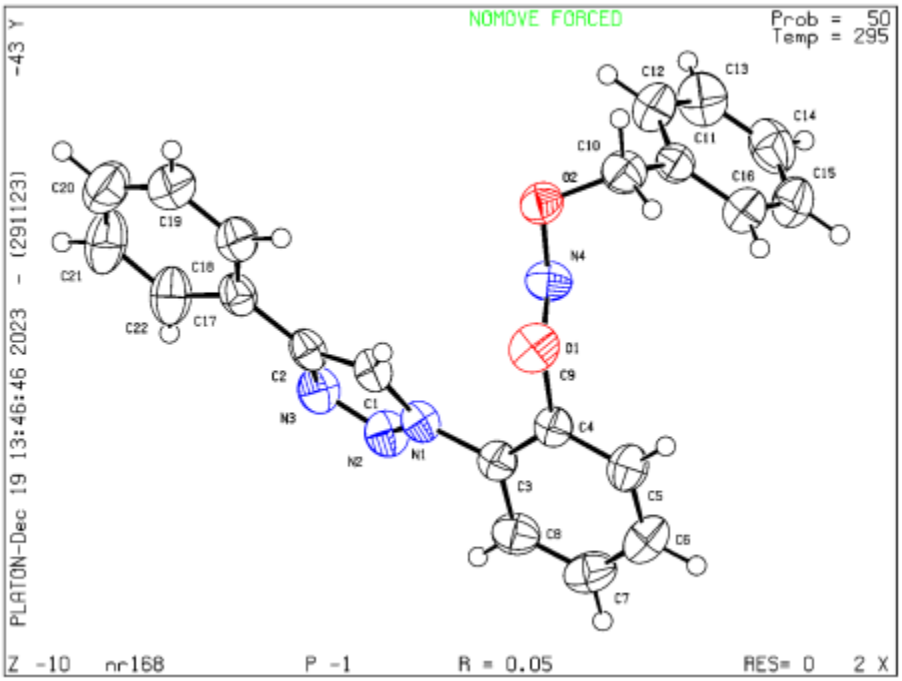
Important bond angles of 2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-*N*-phenylbenzamide

Module	Bond angle (^{o})
N2-N1-C9	117.75(12)
C1-N1-N2	110.42(12)

C1-N1-C9	131.70(12)
N3-N2-N1	106.69(12)
N2-N3-C2	109.76(12)
C15-N4C16	126.52(14)
N1-C1-C2	105.58(13)
N3-C2-C3	121.70(13)
C1-C2-N3	107.50(14)
C1-C2-C3	130.61(15)
C4-C3-C2	121.08(15)
C8-C3-C2	120.27(16)
C8-C3-C4	118.59(17)
C5-C4-C3	120.83(19)
C6-C5-C4	119.0(2)
F1-C6-C7	117.9(3)
C5-C6-F1	119.7(2)
C5-C6-C7	122.4(2)
C6-C7-C8	118.7(2)
C7-C8-C3	120.5(2)
C10-C9-N1	122.04(14)
C14-C9-N1	117.20(14)
C14-C9-C10	120.75(15)
C9-C10-C15	126.47(14)
C11-C10-C9	117.31(15)
C11-C10-C15	116.17(14)
C12-C11-C10	122.06(17)
C11-C12-C13	119.71(17)
C12-C13-C14	119.93(18)
C13-C14-C9	120.19(17)

O1-C15-N4	123.52(15)
O1-C15-C10	119.60(13)
N4-C15-C10	116.84(13)
C17-C16-N4	117.58(15)
C21-C16-N4	123.26(15)
C21-C16-C17	119.08(16)
C18-C17-C16	120.00(18)
C17-C18-C19	120.9(2)
C20-C19-C18	119.1(2)
C19-C20-C21	120.9(2)
C20-C21-C16	119.98(18)

Crystal sample preparation of 6h



Crystal of **6h** was prepared by using dichloromethane and pentane as solvent, the solution of which was kept at room temperature for a period of 4 days to get the single crystal.

Characterization

Table S10: Crystallographic data and the structure refinement detail for *N*-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide

Name	*N*-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide
Formula	$C_{22}H_{18}N_4O_2$
Formula weight	370.40
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	8.7311(8)
b (Å)	9.2400(7)
c (Å)	12.1350(8)
α (°)	98.305(6)
β (°)	97.293(7)
γ (°)	105.502(7)
V (Å^3)	919.32(13)
Z	2
Density(calcd) (g/cm^3)	1.338
Abs. coeff. (mm^{-1})	0.089
F(000)	388.0
Crystal size (mm)	0.26 × 0.14 × 0.06
Temperature (K)	295 (2)
Radiation (Å)	0.71073
θ Min, Max (°)	7.564, 58.542
Data set	4315/0/257
R (int)	0.0922
N_{ref}, N_{par}	4315, 257
R, wR_2, S	0.0506, 0.1226, 1.033

Important bond lengths of *N*-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide

Bond distances	
Module	Bond distance (Å)
O1-C9	1.2179(19)
O2-N4	1.3919(17)
O2-C10	1.448(2)
N1-N2	1.3537(18)
N1-C1	1.345(2)
N1-C3	1.428(2)
N2-N3	1.3071(19)
N3-C2	1.358(2)
N4-C9	1.331(2)
C1-C2	1.364(2)
C2-C17	1.461(2)
C3-C4	1.391(2)
C3-C8	1.387(2)
C4-C5	1.389(2)
C4-C9	1.503(2)
C5-C6	1.372(2)
C6-C7	1.376(3)
C7-C8	1.369(3)
C10-C11	1.491(3)
C11-C12	1.378(3)
C11-C16	1.372(2)
C12-C13	1.375(3)
C13-C14	1.366(3)
C14-C15	1.365(3)
C15-C16	1.378(3)

C17-C18	1.380(3)
C17-C22	1.387(2)
C18-C19	1.372(3)
C19-C20	1.368(3)
C20-C21	1.359(3)
C21-C22	1.378(3)

Important bond angles of *N*-(benzyloxy)-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzamide

Module	Bond angle (^{o})
N4-O2-C10	108.30(12)
N2-N1-C3	118.09(13)
C1-N1-N2	110.28(13)
C1-N1-C3	131.59(13)
N3-N2-N1	106.51(13)
N-N3-C2	110.17(13)
C9-N4-O2	119.58(15)
N1-C1-C2	105.78(14)
N3-C2-C1	107.26(14)
N3-C2-C17	121.36(14)
C1-C2-C17	131.36(16)
C4-C3-N1	121.62(14)
C8-C3-N1	118.07(15)
C8-C3-C4	120.31(15)
C3-C4-C9	126.26(14)
C5-C4-C3	118.14(15)
C5-C4-C9	115.58(14)
C6-C5-C4	121.31(17)

C5-C6-C7	119.85(17)
C8-C7-C6	120.17(18)
C7-C8-C3	120.21(17)
O1-C9-N4	125.21(16)
O1-C9-C4	121.89(17)
N4-C9-C4	112.71(15)
O2-C10-C11	113.40(14)
C12-C11-C10	121.40(16)
C16-C11-C10	120.47(18)
C16-C11-C12	118.12(19)
C13-C12-C11	120.76(18)
C14-C13-C12	120.6(2)
C15-C14-C13	119.2(2)
C14-C15-C16	120.5(2)
C11-C16-C15	120.9(2)
C18-C17-C2	121.16(15)
C18-C17-C22	118.23(17)
C22-C17-C2	120.61(16)
C19-C18-C17	120.86(18)
C20-C19-C18	120.3(2)
C21-C20-C19	119.7(2)
C20-C21-C22	120.72(19)
C21-C22-C17	120.2(2)