Supplementary Information (SI) for RSC Advances.
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Green One-Pot Synthesis of Quinoxaline Derivatives Using Sulfo-Anthranilic Acid Functionalized Alginate-$MCFe_2O_4$ Nanostructures: A Novel Superparamagnetic Catalyst with Antiproliferative Potential

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1. Supporting results

1.1. Materials and methods

All starting materials and chemicals used in this research were bought from the Sigma-Aldrich chemical company and applied without further purification. Melting points were measured using an Electrothermal 9200 apparatus and were uncorrected. Elemental analysis was performed on a Perkin–Elmer 2400 C, H, N analyzer. FT-IR spectra of all samples in our study were recorded in the sub-region 400-4000 cm-1 using potassium bromide discs using a Perkin–Elmer 550 spectrometer. Mass spectra were obtained on an HP 5975 Mass Selective Detector at 70 eV. The ^1H NMR and ^{13}C NMR were performed on Bruker advance spectrometer instrument using $CDCl_3$ and DMSO-d_6 as solvent and tetramethylsilane as internal standard. Thin layer chromatography (TLC) was used in silica gel polygram SILG/ V 254 nm plates. The X-ray diffraction (XRD) pattern related to the structural phases of the prepared catalyst was accomplished using a JEOL JSM-6100 microscope with (Cu kα radiation, λ=1.54 Å) in the region of 2Θ = 10°- 80°. The surface morphology of the $MCFe_2O_4$@Alginate@SAA nanocatalyst was studied by SEM (Hitachi S4160 scanning electron microscopy). The elemental mapping and compositional analysis were performed by energy-dispersive X-ray spectroscopy (EDX) by a Kevex, Delta Class I, equipped with the SEM instrument. A varying magnetic field from -10000 to 10000 Oe on a BHV-S5 vibrating sample magnetometer (VSM) was utilized at room temperature to characterize the magnetic measurement of

modified and unmodified nanoparticles. The nanocatalyst's transmission electron microscope (TEM) images were performed using an FEI CM200 field emission at an accelerating voltage of 200 kV. The thermal gravimetric analysis (TGA) of the nano-magnetic solid acid catalyst was carried out on a Shimadzu Thermogravimetric Analyzer (TG-50) in the temperature range of 25-800 ^{o}C at a heating rate of 10 ^{o}C /min in the air under N_2 atmosphere.

In order to determine the catalytic behavior of $MCFe_2O_4$@Alginate@SAA, the proposed mechanism for the formation of compound (**4a-x**) is the following (**SCHEM 1**).

1.2. Proposed Reaction Mechanism for One-Pot Multicomponent Knoevenagel-Shift Base Reactions

In **Scheme 3**, we delineate a plausible reaction mechanism for the one-pot multicomponent Knoevenagel-shift base reactions mediated by MFe_2O_4@PDA@$BuSO_3H$ magnetic nanoparticles (MNPs). Although the precise mechanistic pathway may not be fully elucidated, we hypothesize the involvement of various catalytic interactions.

Mechanistic Steps Overview:

1. **Activation of the Nanocatalyst Surface:** The surface of MFe_2O_4@PDA@$BuSO_3H$ is rich in -SO_3H functional groups, which play a pivotal role in the initial phase. Coordination between these sulfonic acid groups and the electron-rich sites on the aldehydes and substituted bromoacetophenones enhances the reactivity of the reactants.

2. **Enhanced Electrophilicity:** The presence of electron-deficient sites on the catalyst surface amplifies the electrophilic nature of the carbonyl carbon atoms. This activation is crucial for the subsequent nucleophilic attack, as it makes the carbonyls significantly more reactive.

3. **Formation of an Intermediate Complex:** A transient complex forms between the nanocatalyst and the carbonyl compound, stabilizing the activated state and facilitating further reaction steps.

4. **Nucleophilic Attack by Guanidine:**The guanidine derivative's amino group performs a nucleophilic attack on the electrophilic carbonyl carbon, leading to the formation of an imine intermediate through a condensation reaction.

5. **Release of the Imine Intermediate:**Once the imine is formed, it dissociates from the catalyst's surface, allowing the catalyst to remain available for additional cycles.

6. **Secondary Imine Formation:**A nucleophilic attack by aminoguanidine on a subsequent carbonyl carbon results in another imine intermediate, further extending the reaction pathway.

7. **Intramolecular Proton Transfer and Rearrangement:**The imine intermediate undergoes proton transfer and bond rearrangements, stabilizing its structure and enabling further reactions.

8. **Formation of the Aminoimidazole Ring:**The interaction between th bromoacetophenone derivative and the imine compound facilitates ring closure, creating the aminoimidazole structure characteristic of the final products.

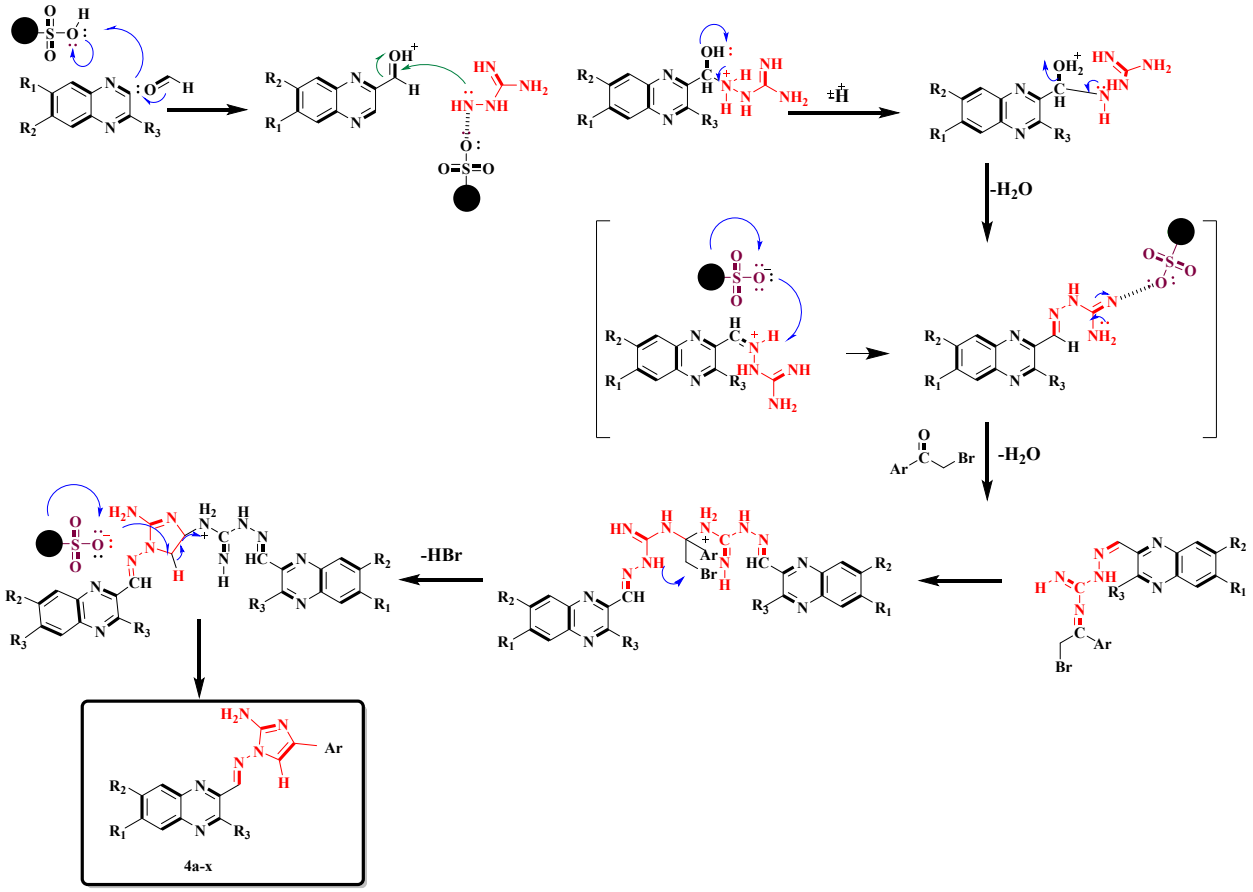
9. **Stoichiometry of Reactants:**Notably, two equivalents of the imine compound are required for each equivalent of the α-bromo compound, underscoring the stoichiometric dependencies within the reaction.

10. **Final Cyclization and Product Release:**The cycle culminates in the expulsion of excess imine compound, resulting in the release of the desired final derivative while regenerating the active catalyst.

Role of the MFe_2O_4@PDA@$BuSO_3H$ Nanocatalyst

The MFe_2O_4@PDA@$BuSO_3H$ nanocatalyst, through its functionalized sulfonic acid (-SO_3H) groups, introduces Lewis's acid sites that significantly enhance the reaction kinetics. The coordination of these acid sites with the electron-rich oxygen atoms in carbonyl groups amplifies the electrophilicity of these centers, thus facilitating nucleophilic attack by amines.

Additionally, the catalyst stabilizes the negative charges on reaction intermediates, effectively lowering the activation energy required for the reaction and accelerating the overall process. By ensuring proper orientation of reactants near the active sites of the nanocatalyst, the MNPs optimize the imine formation step and promote efficient transformation to the final product.The catalyst's ability to facilitate reaction through adsorption and desorption processes further enhances its effectiveness, enabling the efficient cycle of catalysis while remaining structurally intact for subsequent uses.



SCHEME 1. The proposed mechanism for the preparation of compounds (**4a-x**)

1-3.The analytical and spectroscopic data for the unknown final products

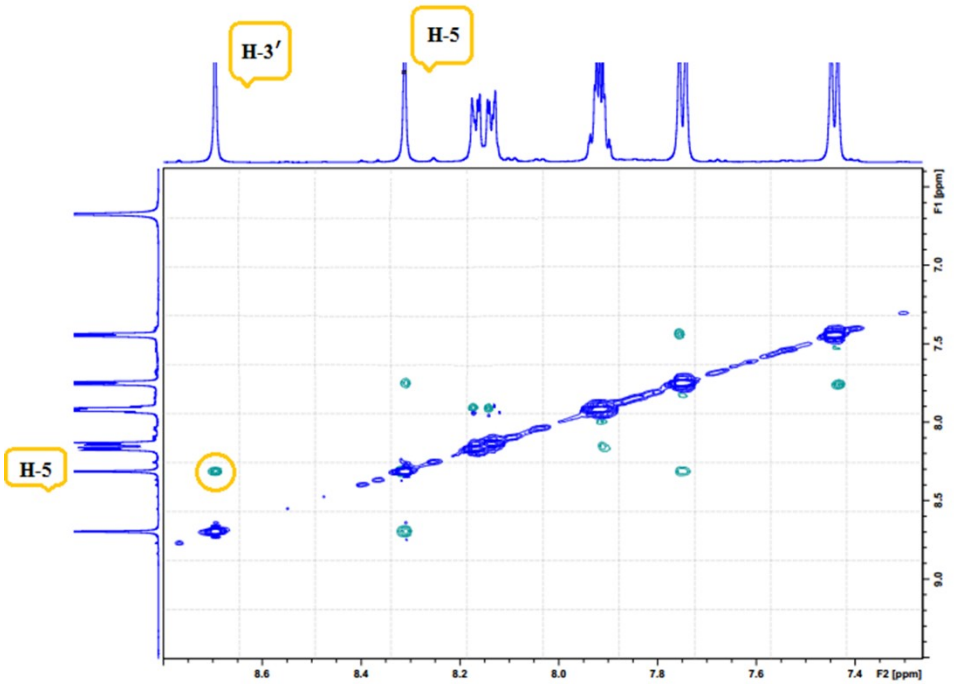


FIGURE S1. The (H-H) ROESY spectrum of compounds **4d**

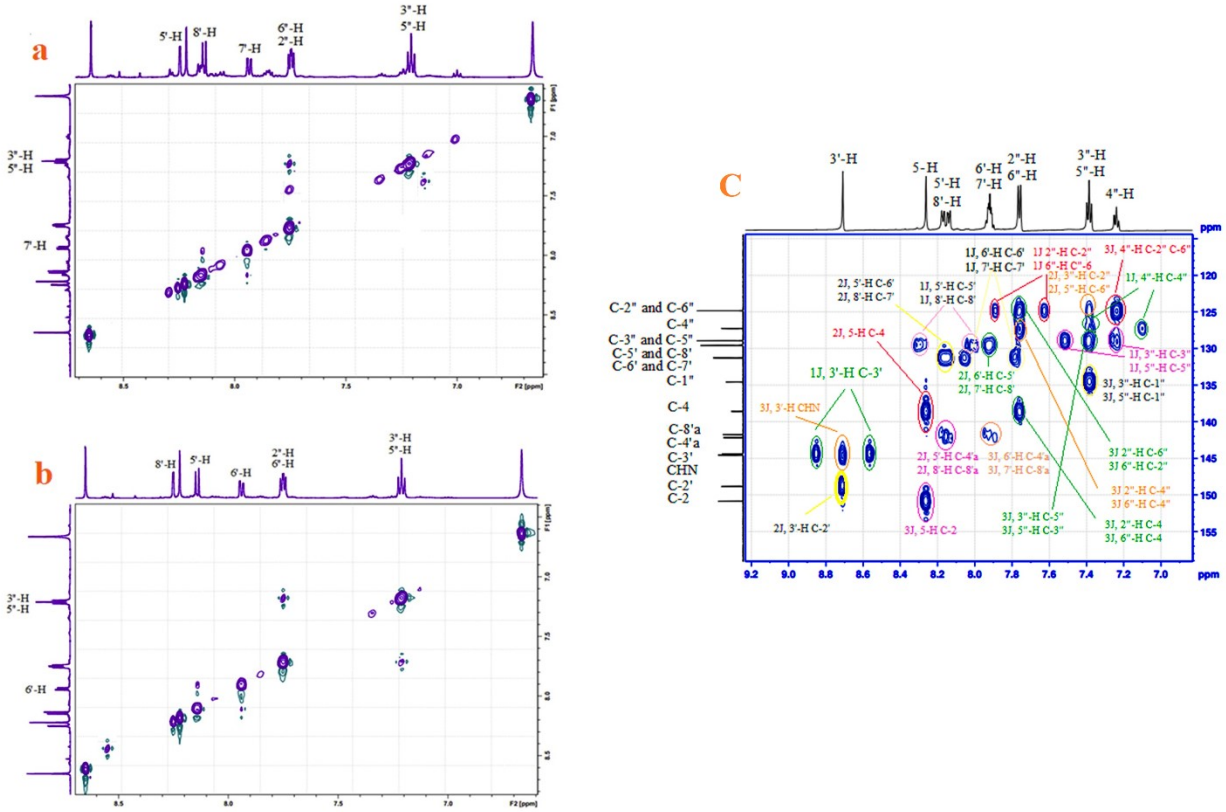
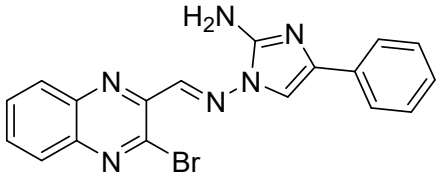


FIGURE S2. The (H-H) COSY spectrum of compounds **4m** and **4n** (a, b) and the HMBC spectrum of compounds **4a** (C).

4.1.1.1. (E)-4-phenyl-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine(8a)

IR (KBr, cm^{-1}) ν_{max}: 3467 and 3298 (NH str.), 3217, 3136 and 3062 (CH str.), 1651, 1472, 1173, 765, 692, cm^{-1};^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.56 (s, 1H, CHN), 8.32 (s, 1H, 5-H), 7.67-7.69 (m, 2H, 6′-H and 7′-H), 8.29-8.32 (m, 2H, J = 7.5 Hz, 2″-H and 6″-H), 7.87-7.89 (d, 2H, 5′-H and 8′-H), 7.60 (t, 2H, J = 7.5 Hz, 3″-H and 5″-H), 7.40 (t, 1H, J = 7.6 Hz, 4″-H),6.88 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.1 (C-2), 150.55 (C-2′), 146.4 (CHN), 143.6 (C-3′), 142.07 (C-4′a), 140.6 (C-4), 134.5 (C-1″), 139.19 (C-6′ and C-7′), 136.30 (C-5′ and C-8′), 132.14 (C-3″ and C-5″), 131.81 (C-4″), 129.36 (C-2″ and C-6″), 126.75 (C-8′a), 107.64(C-5).



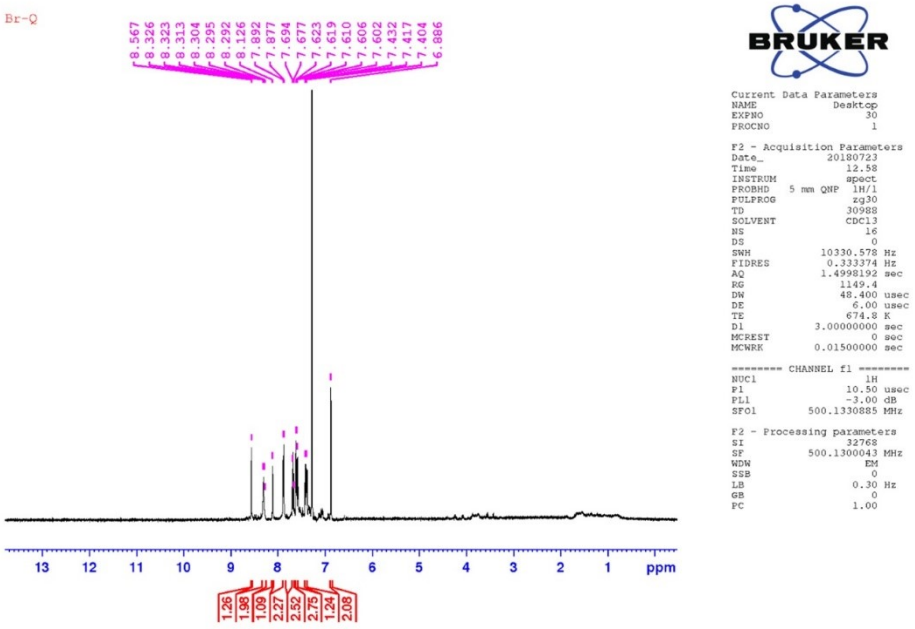


Figure S3. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **8a**.

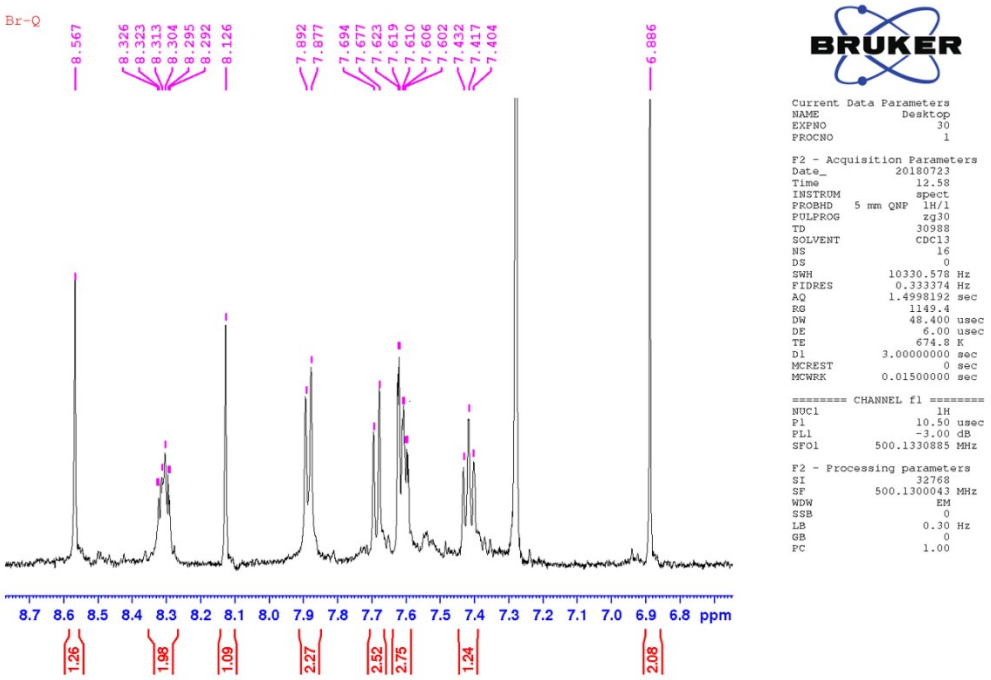


Figure S4. Expand ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **8a.**

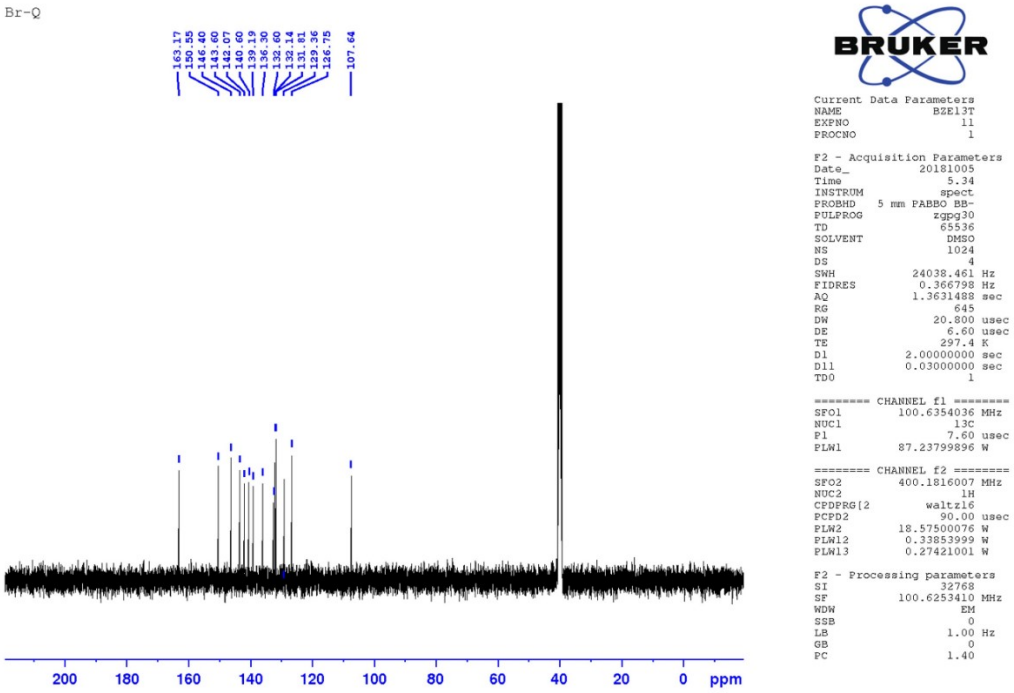
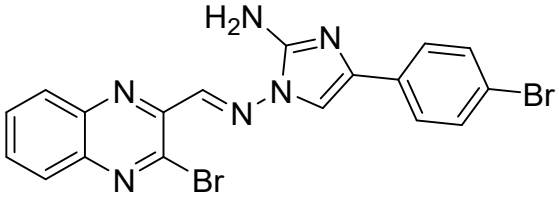


Figure S5. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8a.**

4.1.1.2. (E)-4-(4-bromophenyl)-1-(((3-bromoquinoxalin-2-yl)methylene)amino)-1H-imidazol-2-amine (8b)

IR (KBr): 3412 and 3274 (NH str.), 3204, and 3062 (CH str.), 14741, 1177, 754, 676, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$-d_6) δ: 9.59 (s, 1H, CHN), 8.82 (s, 1H, 3′- H), 7.79-7.81 (d, 2H, 5′-H and 8′-H), 7.54-7.56 (dd, 2H, J = 8.4 Hz, 2″-H and 6″-H), 7.57-7.58 (dd, 2H, J = 8.4 Hz, 3″-H and 5″-H), 7.34-7.36 (m, 2H, 6′-H and 7′-H), 6.69 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.3 (C-2), 148.8 (C-2′),146.6(CHN), 144.7 (C-3′),143.1 (C-4′a), 140.9 (C-8′a), 138.3 (C-4), 132.8 (C-1″), 131.2(C-3″ and C-5″), 130.0 (C-5′ and C-8′), 129.1 (C-6′ and C-7′), 127.5 (C-2″ and C-6″), 123.2 (C-4″),109.7 (C-5); MS:(m/z) M^+ calcd. for $C_{18}H_{13}BrN_6$: 392.0, Found: 392.0



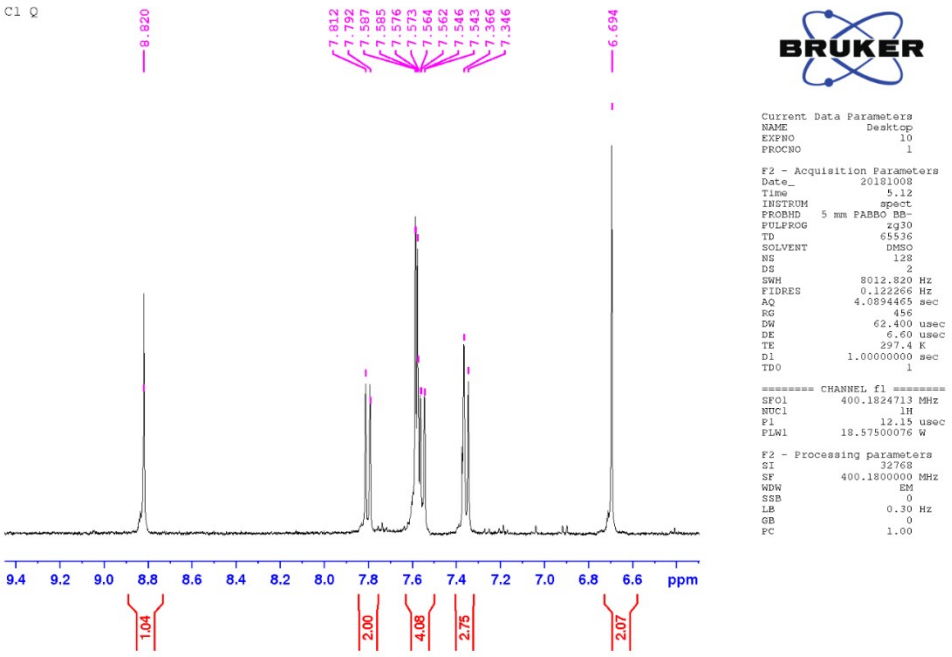


Figure S6. Expand ^1H NMR spectrum (400 MHz, DMSO-d_6) of **8b.**

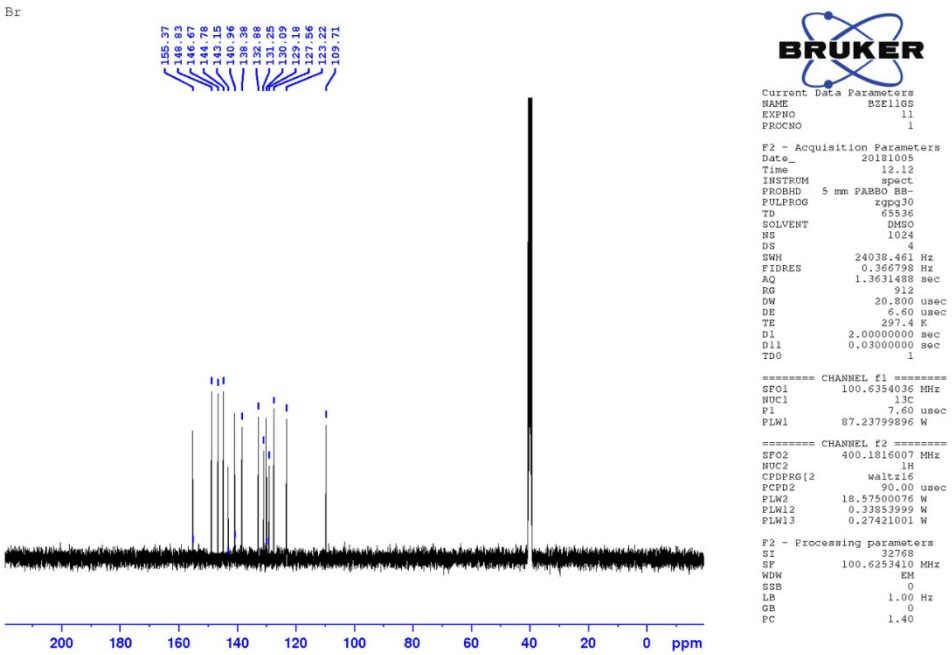
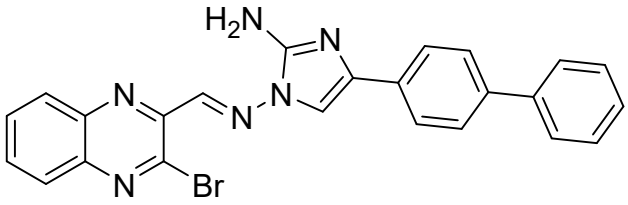


Figure S7. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8b.**

4.1.1.3. (E)-4-([1,1'-biphenyl]-4-yl)-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine (8c)

IR (KBr): 3406and 3274 (NH str.), 3204, and 3051 (CH str.), 1636, 1462, 1168, 755, 672 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.83 (s, 1H, CHN), 8.17 (s, 1H, 5- H), 8.02-8.04 (d, 2H, J = 7.86, 6′-H and 7′-H), 8.12-8.17 (m, 2H, J = 8.2 Hz, 2″-H and 6″- H), 7.98-8.0 (d, 2H, 5′-H and 8′-H),7.90-7.92 (m, 4H, 3″-H, 5″-H, H-2 phenyl and H-6 phenyl), 7.28-7.34 (dd, 2H, J = 7.5 Hz, H-3 phenyl and H-5 phenyl), 7.12-7.16 (dd, 1H, J = 7.5, H-4 phenyl),6.69 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.3 (C-2), 148.8 (C-2′), 146.04 (CHN), 144.0 (C-3′),141.8 (C- 4′a), 139.9 (C-4), 138.20 (C-8′a), 136.3 (C-4″), 135.4 (C-1 phenyl), 133.6 (C-1″), 132.1 (C-6′ and C-7′), 129.1 (C-5′ and C-8′), 128.5 (C-3 and C-5 phenyl), 127.4 (C-4 phenyl), 125.7 (C-2″and C-6″), 123.9 (C-2 and C-6 phenyl), 122.7 (C-3″ and C-5″),110.2 (C-5); MS:(m/z) M^+ calcd. for $C_{24}H_{18}N_6$: 390.1, Found: 390.1



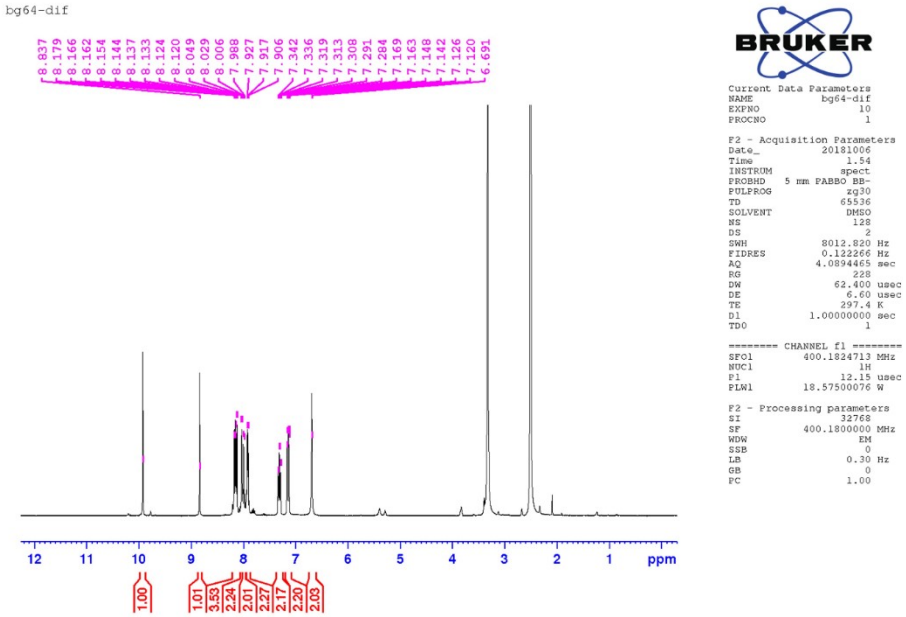


Figure S8. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8c**.

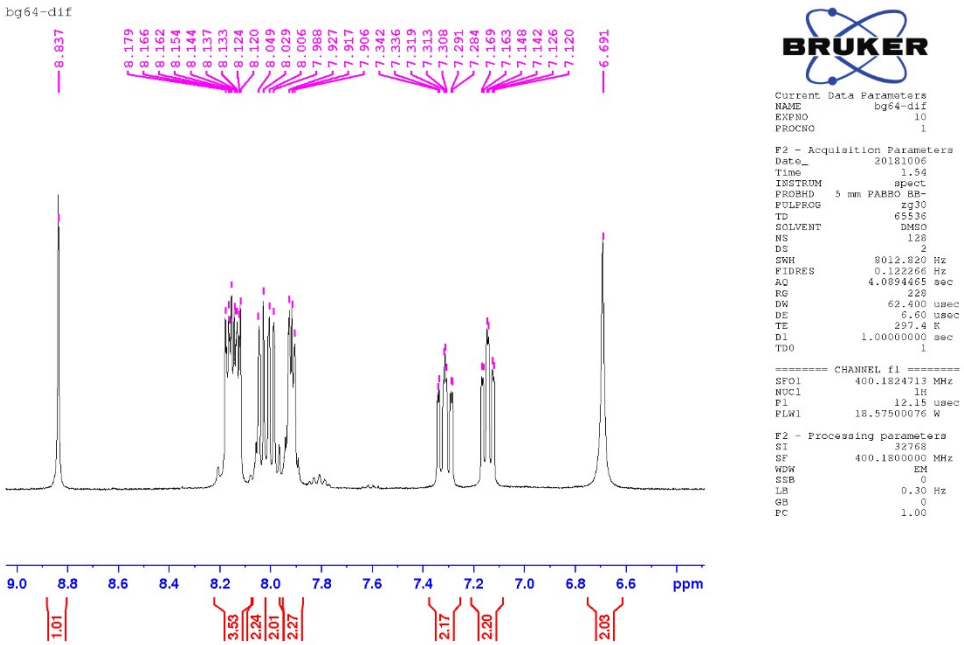


Figure S9. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8c** (Table 2, entry 3)**.**

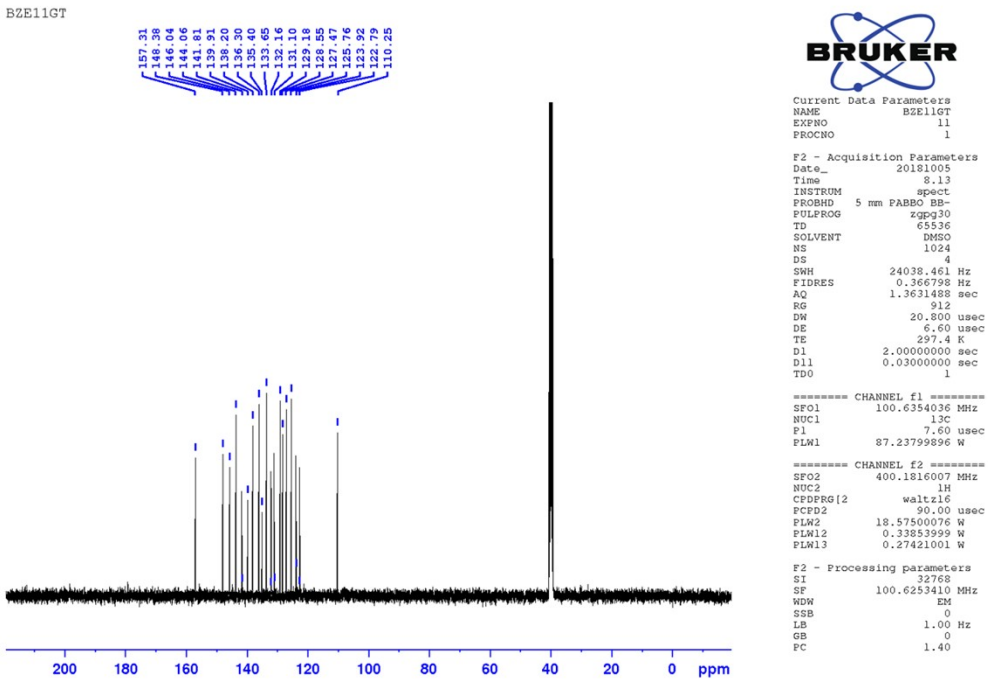
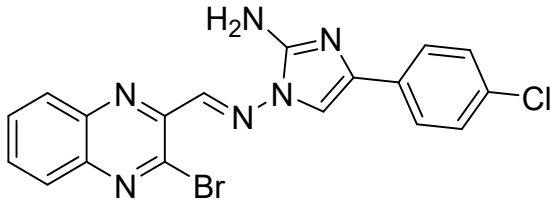


Figure S10. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8c.**

4.1.1.4. (E)-1-(((3-bromoquinoxalin-2-yl)methylene)amino)-4-(4-chlorophenyl)-1H-imidazol-2-amine (8d)



IR (KBr): 3466 and 3295 (NH str.), 3214, and 3085 (CH str.),1652, 1471, 1225, 766, 675 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.95 (s, 1H,CHN), 8.66 (s, 1H, 5-H), 7.79-7.81 (d, 2H, 5′-H and 8′-H), 7.57-7.58 (d, 2H, 6′-H and 7′-H), 7.65-7.67 (dd, 2H, J = 8.4 Hz, 6″-H, 2″-H), 7.44 (d, 2H, J = 8.4 Hz, 3″-H and 5″-H),6.71 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 155.4 (C-2), 148.8 (C-2′), 146.1(CHN), 144.7 (C-3′), 141.9 (C-4′a), 141.0 (C-8′a), 137.8 (C-4), 133.9 (C-1″), 131.4 (C-4″), 130.8 (C-6′ and C-7′), 129.6 (C-5′ and C-8′), 128.6 (C-3″ and C-5″), 124.4 (C-2″ and C-6″),111.2 (C-5); MS:(m/z) M^+ calcd. for $C_{13}H_{18}ClN_6$: 348.0, Found: 348.0

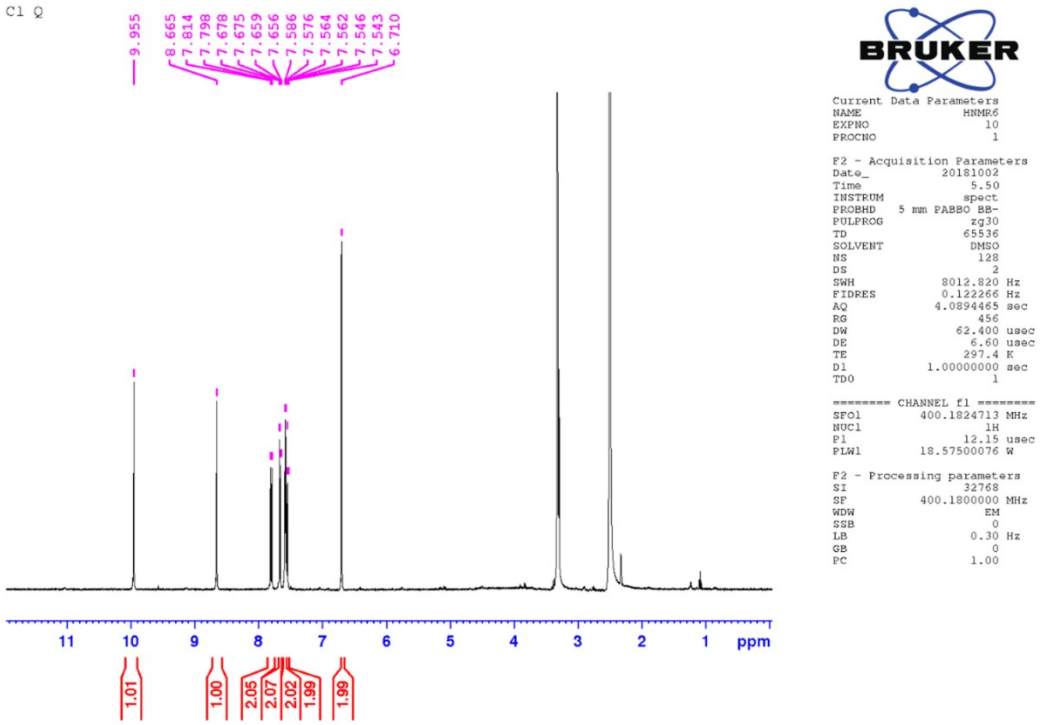


Figure S11. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8d**.

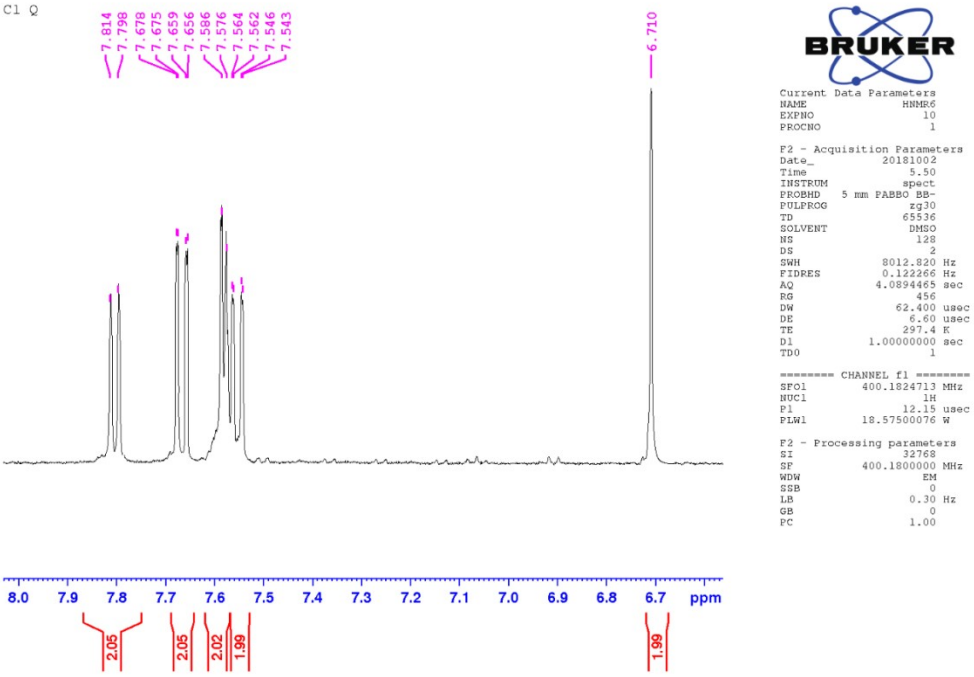


Figure S12. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8d.**

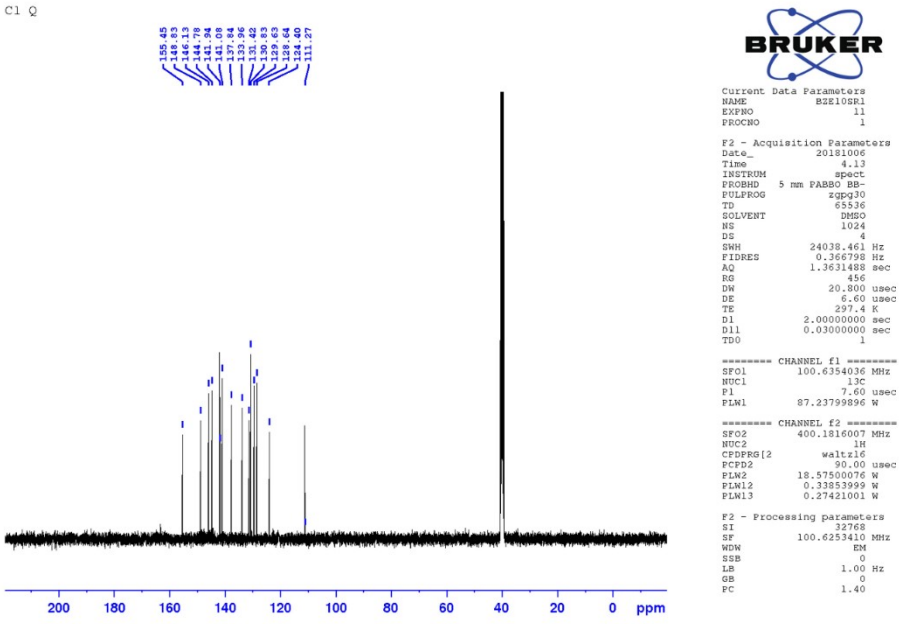
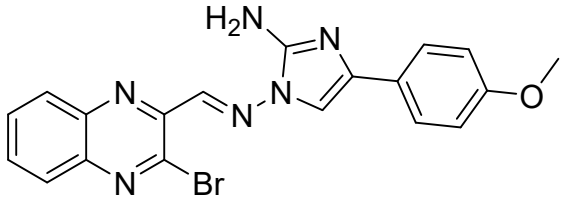


Figure S13. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8d.**

4.1.1.5. (E)-4-(4-methoxyphenyl)-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine (8e)

IR (KBr): 3454 and 3289 (NH str.), 3215, and 3082 (CH str.), 1651, 1473, 1242, 751, 675 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ: 8.20 (s, 1H, CHN), 8.11 (s, 1H, 5-H), 7.94-7.81 (d, 2H, 5′- H and 8′-H), 7.34-7.36 (d, 2H, 6′-H and 7′-H), 7.57 (d, 2H, J = 8.6 Hz, 2″-H and 6″-H), 7.54 (d, 2H, J = 8.6 Hz, 3″-H and 5″-H), 690 (s, 2H, NH_2), 3.78 (s, 3H, Me); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.1 (C-4″), 155.4 (C-2), 149.7 (C-2′), 146.1 (CHN), 144.1 (C-3′),141.9 (C-4′a), 141.7 (C-8′a), 131.4 (C-4), 130.8 (C-6′ and C-7′), 122.6 (C-5′ and C-8′), 120.8 (C- 1″), 120.66 (C-2″ and C-6″), 118.6 (C-3″ and C-5″), 111.2 (C-5),56.5 (C-Me); MS:(m/z) M^+ calcd. For $C_{19}H_{16}N_6O$: 344.1, Found: 344.1



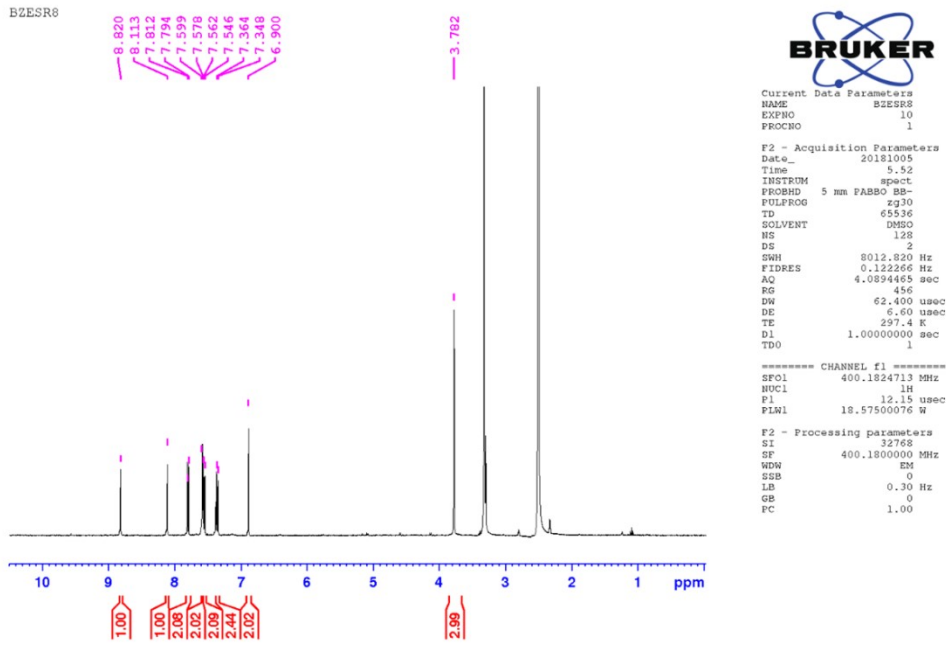


Figure S14. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8e**.

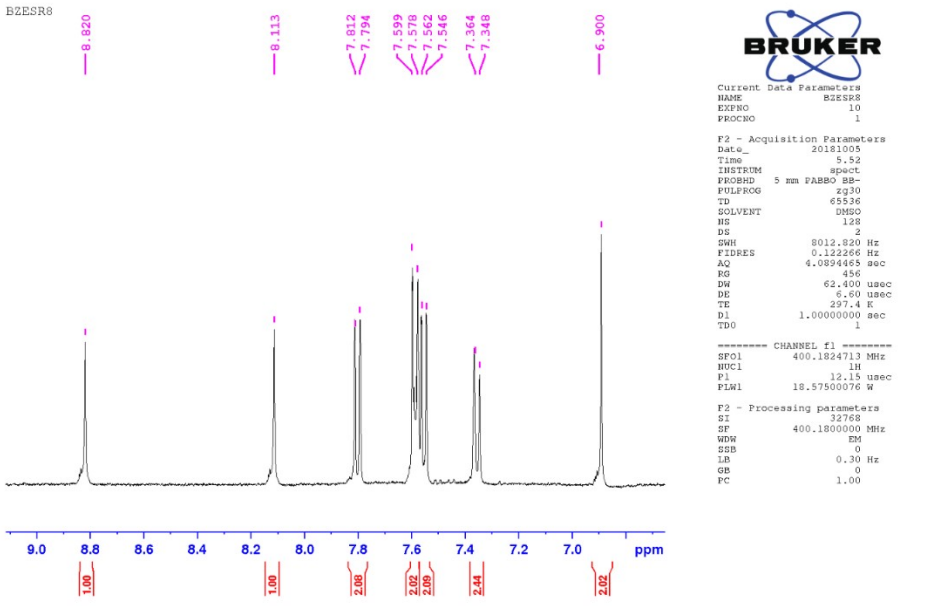


Figure S15. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8e.**

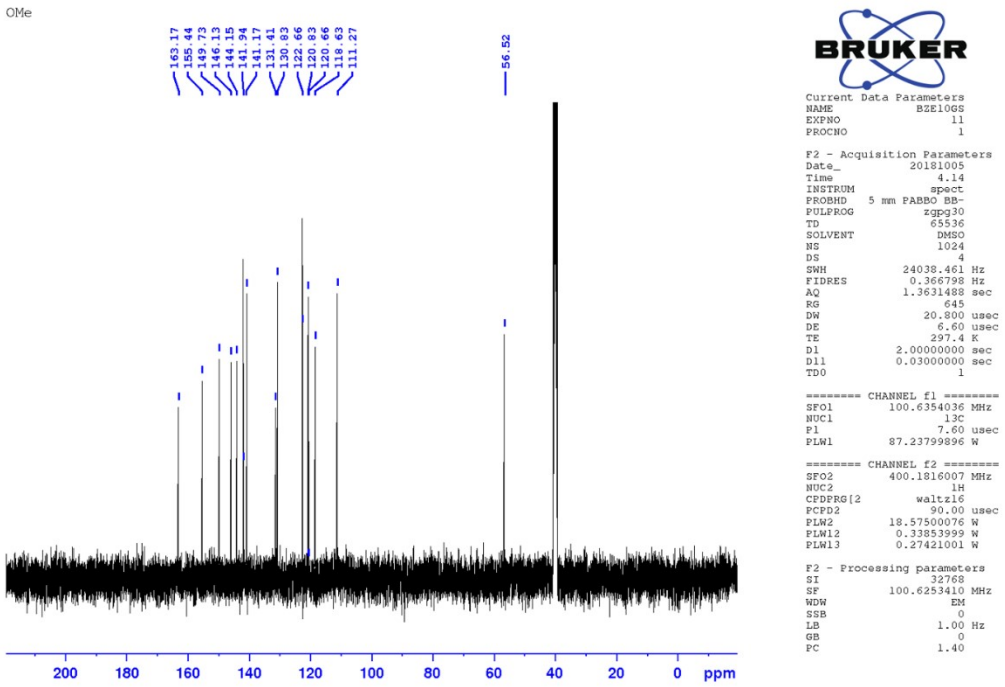
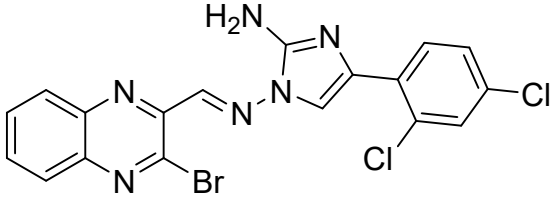


Figure S16. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8e.**

4.1.1.6. (E)-4-(2,4-dichlorophenyl)-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine (8f)

IR (KBr): 3426 and 3304 (NH str.), 3225, 3126 and 3075 (CH str.), 1660, 1471, 1175, 752, 665 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.94 (s, 1H, CHN), 8.69 (s, 1H, 3′- H), 8.31-8.33 (d, 2H, 5′-H, 8′-H), 7.82- 7.84 (d, 2H, 6′-H, 7′-H), 8.24-8.26 (d, 1H, J3″,5″ = 2.4 Hz, 4″-H), 7.70-7.71 (1H, dd, J5″, 6″ = 8.4, J5″,3″ = 2 Hz, 5″-H), 7.43 (s, 1H, 3″-H), 6.70 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO) δ: 163.0 (C- 2), 152.7 (C-2′), 149.0 (C-HN), 147.1 (C-3′), 144.2 (C-4), 142.8 (C-4′a), 140.4 (C-8′a), 137.0 (C- 4″), 135.4 (C-2″), 132.4 (C-3″), 131.7 (C-6″), 126.3 (C-6′ and C-7′), 122.8 (C-5′ and C-8′), 121.42 (C 1″), 120.45 (C-3″),111.5 (C-5); MS: (m/z) M^+ calcd. for $C_{18}H_{12}C_{l2}N_6$: 382.0, Found: 382.2



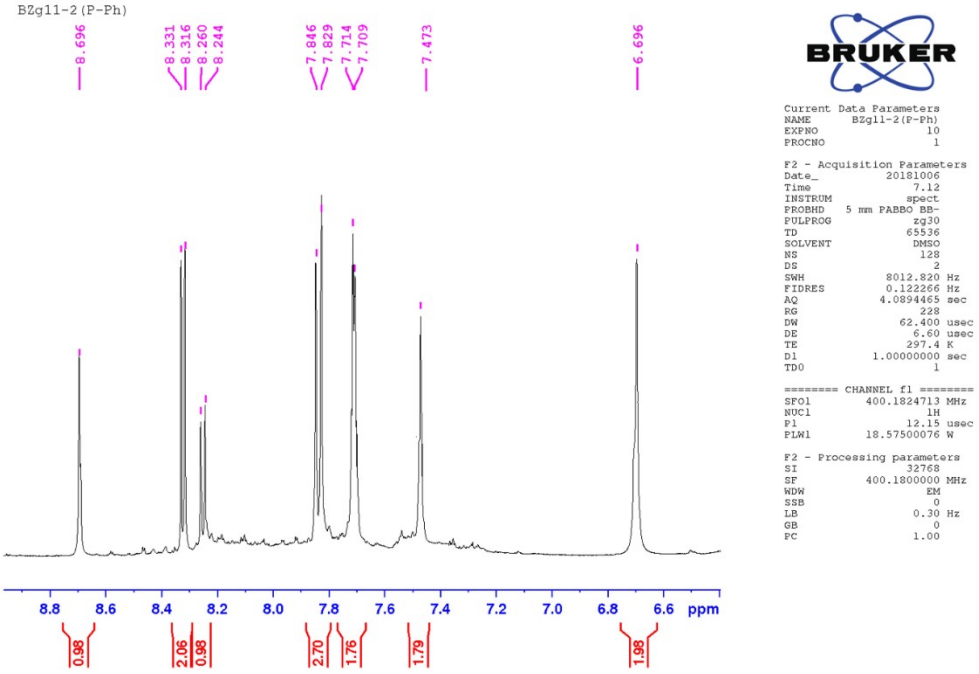


Figure S17. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8f** .

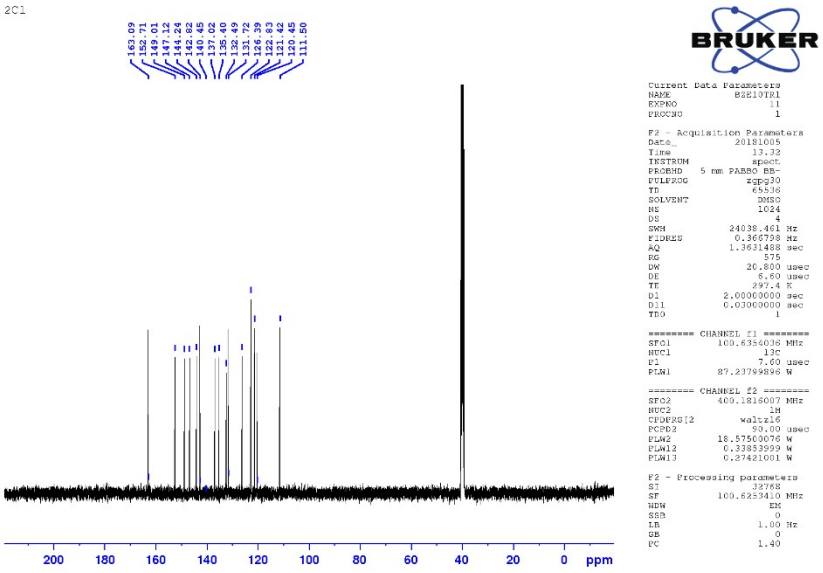
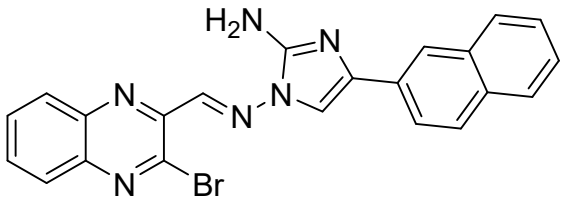


Figure S18. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8f** .

4.1.1.7. (E)-4-(naphthalen-2-yl)-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine (8g)

IR (KBr): 3440 and 3276 (NH str.), 3225, 3142 and 3052 (CH str.), 1651, 1455, 1164, 751, 699 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.81 (s, 1H, CHN), 8.71 (s, 1H, 2″-H), 8.60 (s, 1H, 5-H), 8.14-8.16 (m, 2H, 7″-H and 8″-H), 7.86-7.88 (m, 2H, 4″-H and 5″-H),7.91-7.93 (d, 2H, 5′-H and 8′H), 7.57-7.59 (d, 2H, 6′-H and 7′H), 8.20-8.23 (m, 2H, 3″-H, 6″-H),), 6.77 (s, 2H, NH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 157.3 (C-2), 148.3 (C-2′), 146.0 (C-HN), 144.8 (C-3′), 141.8 (C- 4′a), 139.9 (C-8′a), 138.2 (C-4), 136.3 (C-8″a), 135.4 (C-4″a), 133.6 (C-2″), 132.1 (C- 6′ and C-7′), 131.1 (C-5′ and C-8′), 129.5 (C-5″ and C-8″), 128.5 (C-4″), 127.4 (C-7″), 125.7 (C-6″), 123.9 (C-1″), 122.7 (C-3″),110.2 (C-5); MS: (m/z) M^+ calcd. For $C_{22}H_{16}N_6$: 364.1, Found: 364.0



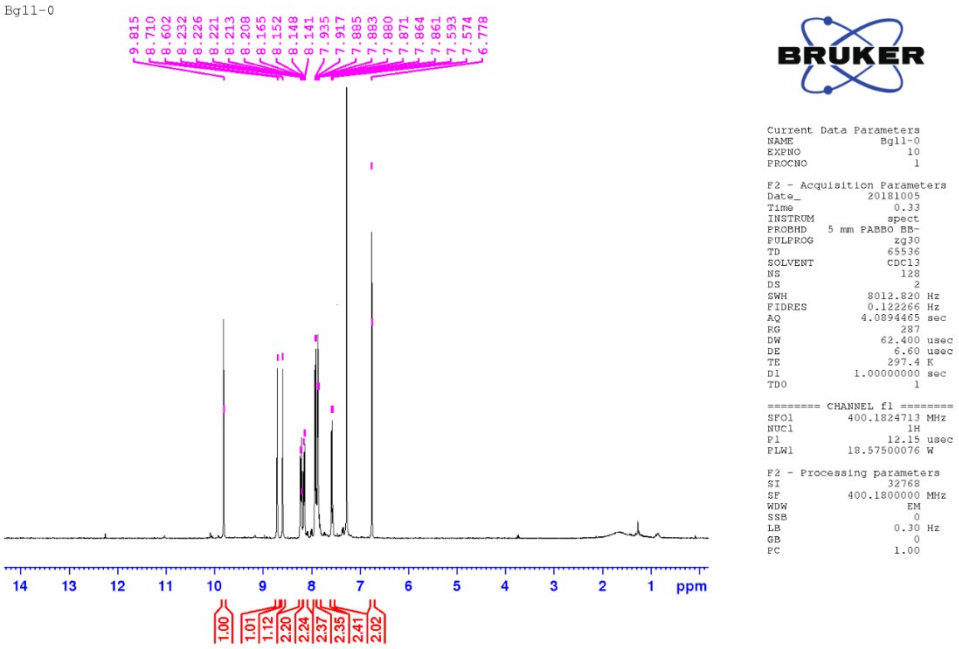


Figure S19. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8g** .

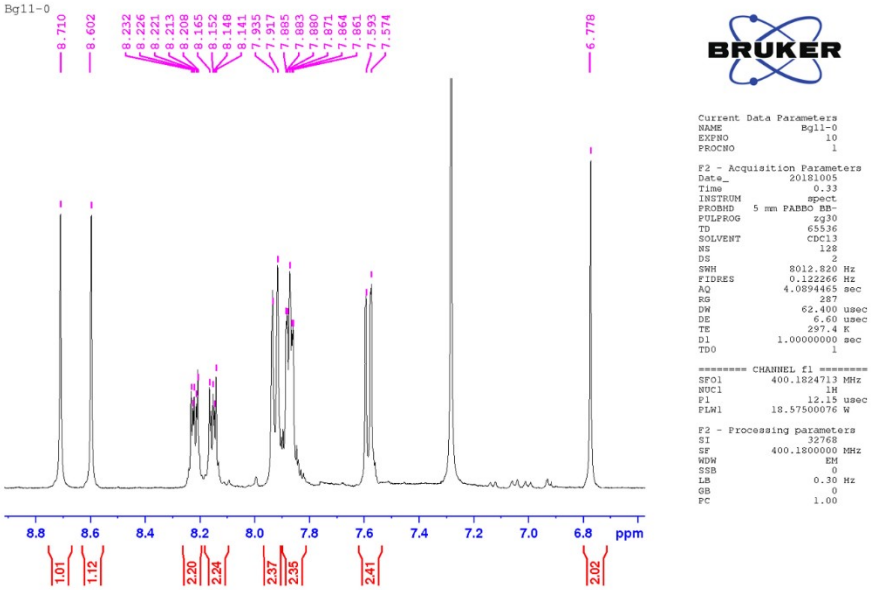


Figure S20. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8g** .

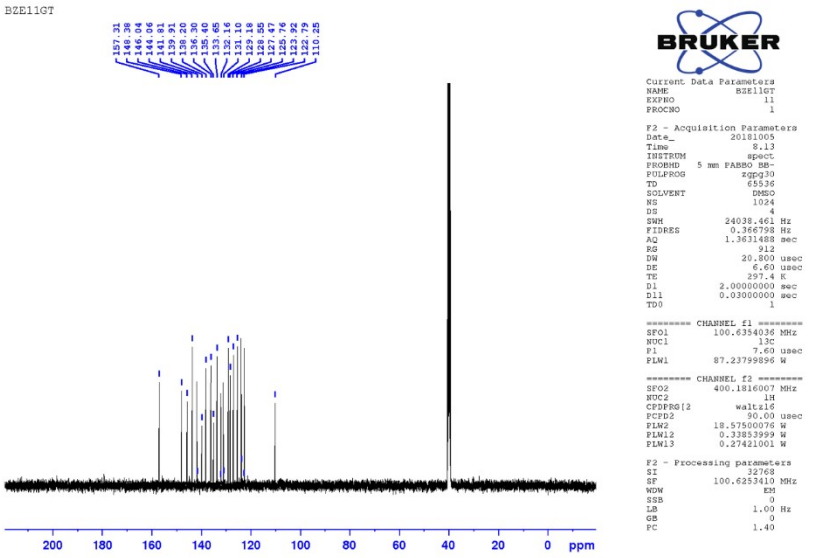
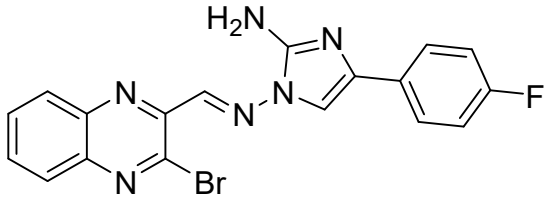


Figure S21. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8g** .

4.1.1.8. (E)-4-(4-fluorophenyl)-1-((quinoxalin-2-ylmethylene)amino)-1H-imidazol-2-amine (8h)

IR (KBr): 3494 and 3316 (NH str.), 3140 (CH str.), 1627, 1454, 1198, 766, 674 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.91 (s, 1H, CHN), 8.11 (ab quartet, 2H, JHH = 8.2 Hz, JHF = 5.7, 6″-H and 2″-H), 7.90 (ab quartet, 2H, JHH = 8.6 Hz, JHF = 8.6 Hz, 3″-H and 5″-H),6.60 (s, 2H, NH_2), 7.63-7.65 (d, 2H, 5′-H and 8′-H), 7.17-7.19 (m, 2H, 6′-H and 7′-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.9 (C-4″), 160.5 (C-1″), 150.7 (C-2), 148.8 (C-2′), 144.5 (C-HN), 144.0 (C-3′), 142.1 (C-4′a), 141.7 (C- 8′a), 136.4 (C-4), 131.2 (C-6′ and C-7′), 129.5 (C-5′ and C-8′), 129.5 (C-2″ and C-6″), 124.8 (C-3″ and C- 5″),101.4 (C-5); MS:(m/z) M^+ calcd. for $C_{18}H_{13}FN_6$: 332.1, Found: 332.1



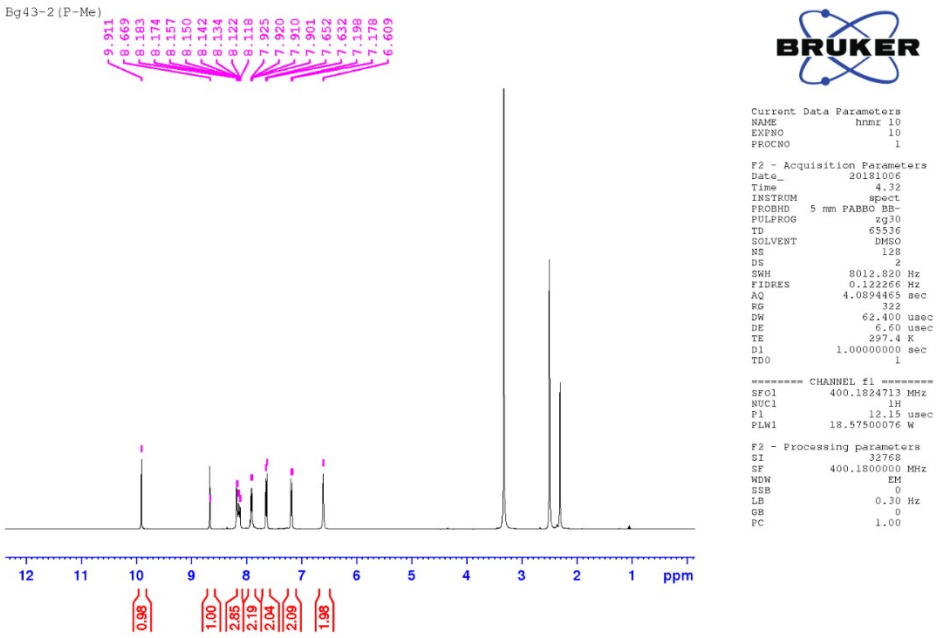


Figure S22. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8h** .

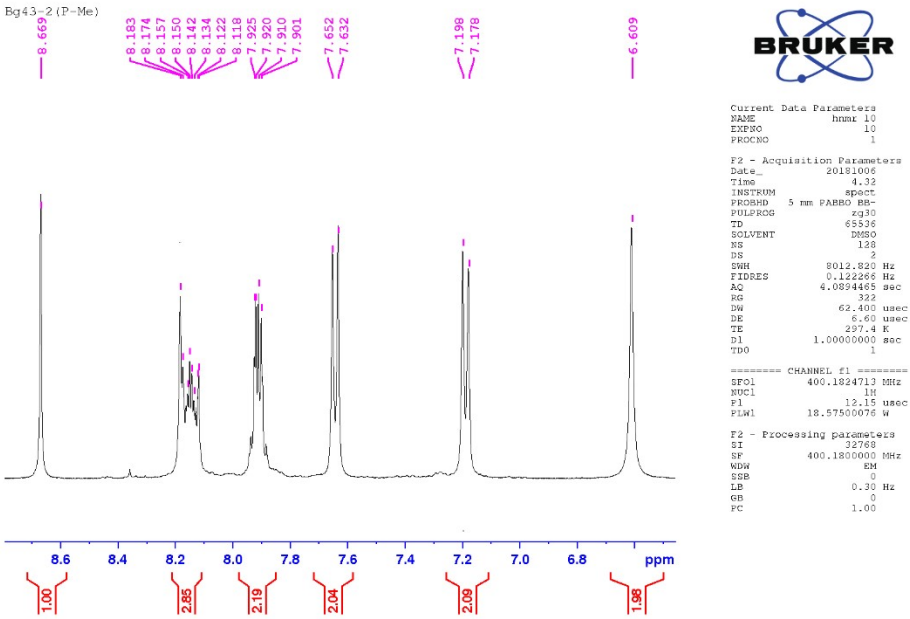


Figure S23. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8h**.

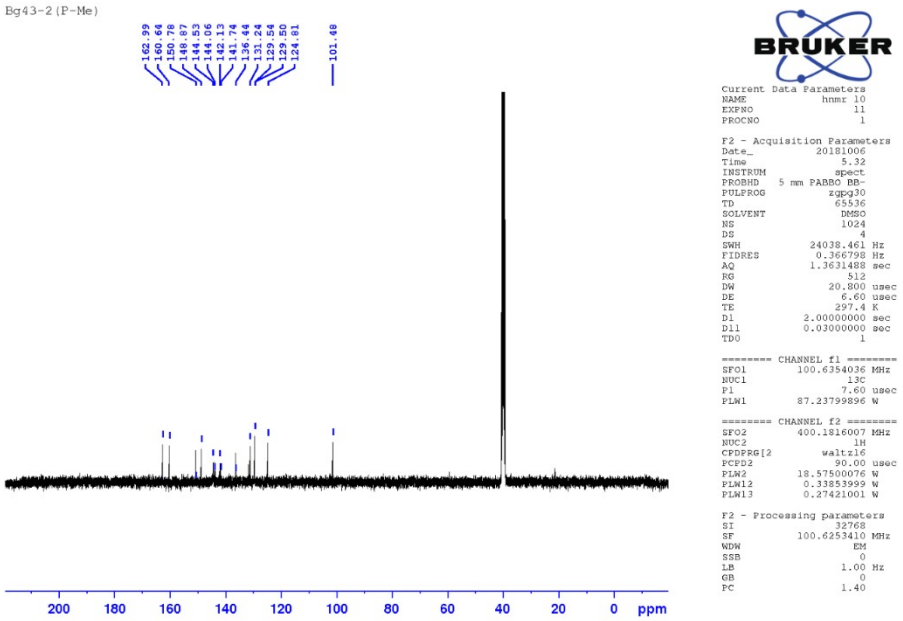
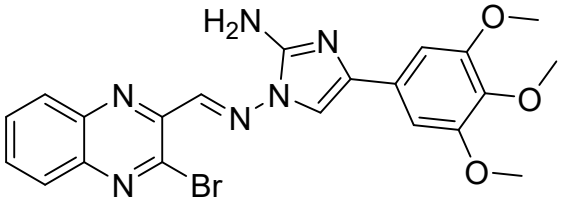


Figure S24. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8h**.

4.1.1.9. (E)-1-((quinoxalin-2-ylmethylene)amino)-4-(3,4,5-trimethoxyphenyl)-1H-imidazol-2- amine (8i)

IR (KBr): 3445 and 3296 (NH str.), 3142 and 3051 (CH str.), 1655, 1472, 11298, 822,756 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.86 (s, 1H, CHN), 8.61 (s, 1H, 3′- H), 8.26-8.32 (m, 2H, 5′-H and 8′-H), 7.58- 7.62 (m, 2H, 6′-H and 7′-H), 7.12 (s, 2H, 2″-H and 6″-H), 6.94 (s, 2H, NH_2), 3.82 (s, 6H, 3″-OMe and 5″-OMe),3.72 (s, 3H, 4″- OMe); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 153.4 (C-3″ and C-5″), 155.3 (C-2), 153.2 (C-2′), 149.8 (CHN), 146.8 (C-3′), 145.4 (C-4′a), 143.1 (C-8′a), 141.71 (C-4), 140.5 (C-4″), 138.9 (C-6′ and C-7′), 130.2 (C-1″), 130.11 (C-5′ and C-8′), 126.85 (C-5), 109.62 (C-2″ and C-6″), 62.20 (C-4″-OMe), 56.5 (C-3″-OMe and C-5″-OMe); MS:(m/z) M^+ calcd. for $C_{21}H_{20}N_6O_3$: 404.1, Found: 404.1



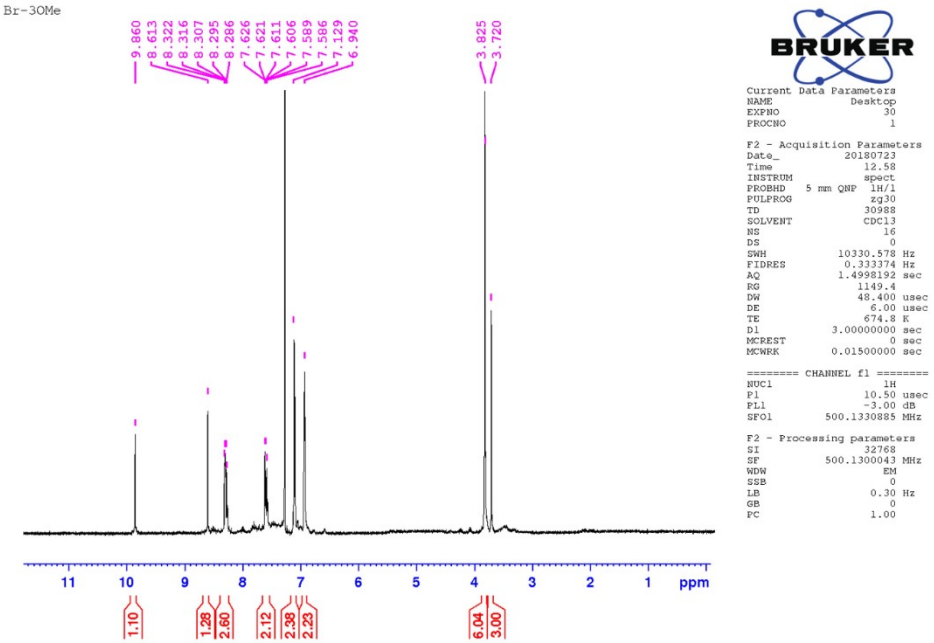


Figure S25. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8i**.

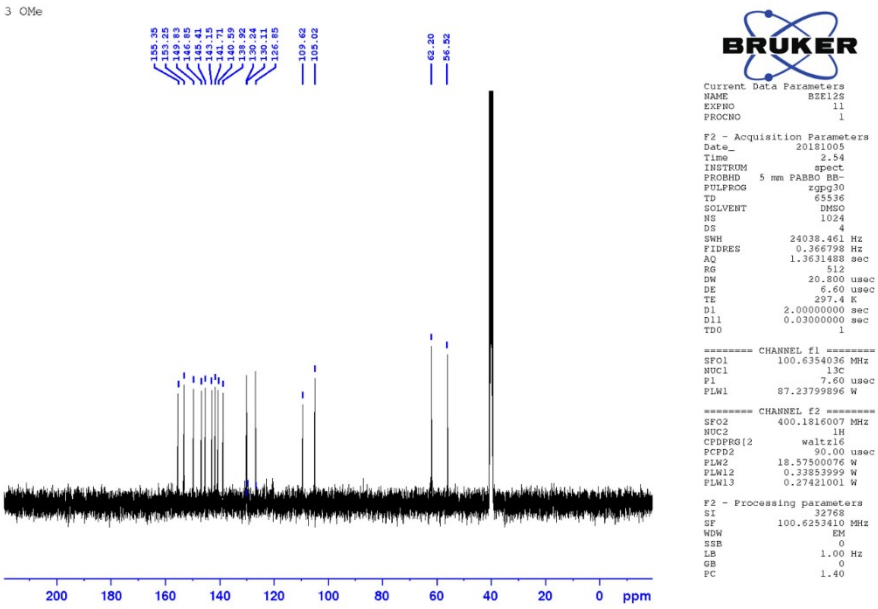


Figure S26. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8i**.

4.1.1.10. (E)-1-((quinoxalin-2-ylmethylene)amino)-4-(thiophen-2-yl)-1H-imidazol-2-amine (8j)

IR (KBr): 3464 and 3282 (NH str.), 3204 and 3061 (CH str.), 1649, 1462, 1171, 766, 697 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.037 (s, 1H, CHN), 8.67 (s, 1H, 3′-H), 7.64-7.66 (m, 2H, 5′-H and 8′-H), 7.40 (d, 1H, J = 4.8 Hz, 5-H thiophenyl), 7.33 (m, 1H, J = 3.2 Hz, 3-H thiophenyl), 7.06 (t, 1H, J = 8.4 Hz, 4-H thiophenyl), 6.91-6.93 (m, 2H, 6′-H and H-7′), 6.71 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.09 (C-2), 148.9 (C-2′), 145.5 (H-3′), 143.9 (CHN), 142.8 (C- 4′a), 141.4 (C-8′a), 138.4 (C-4), 136.3 (C-2 thiophenyl), 132.4 (C-6′ and C-7′), 131.7 (C- 5′ and C-8′), 122.8 (C-5 thiophenyl), 121.4 (C-4 thiophenyl), 120.46 (C-3 thiophenyl), 111.4 (C-5); MS:(m/z) M^+ calcd. for $C_{16}H_{12}N_6S$:320.0, Found: 320.0

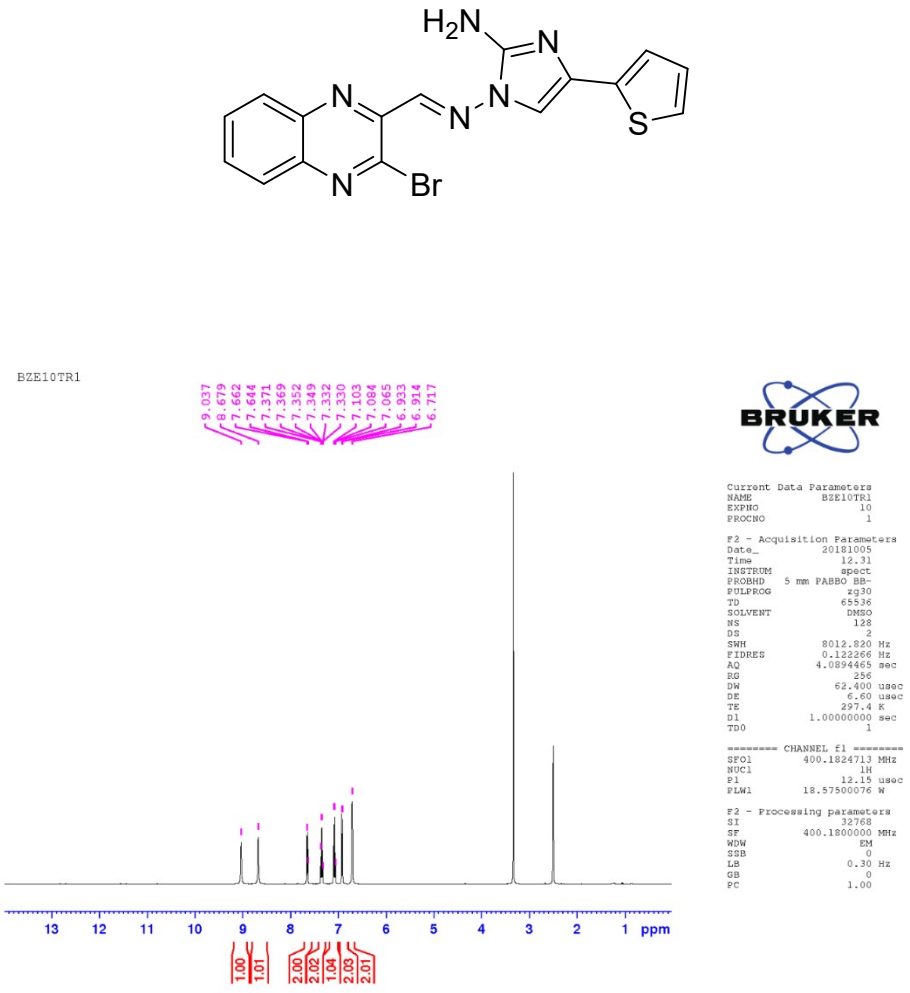


Figure S27. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8j**.

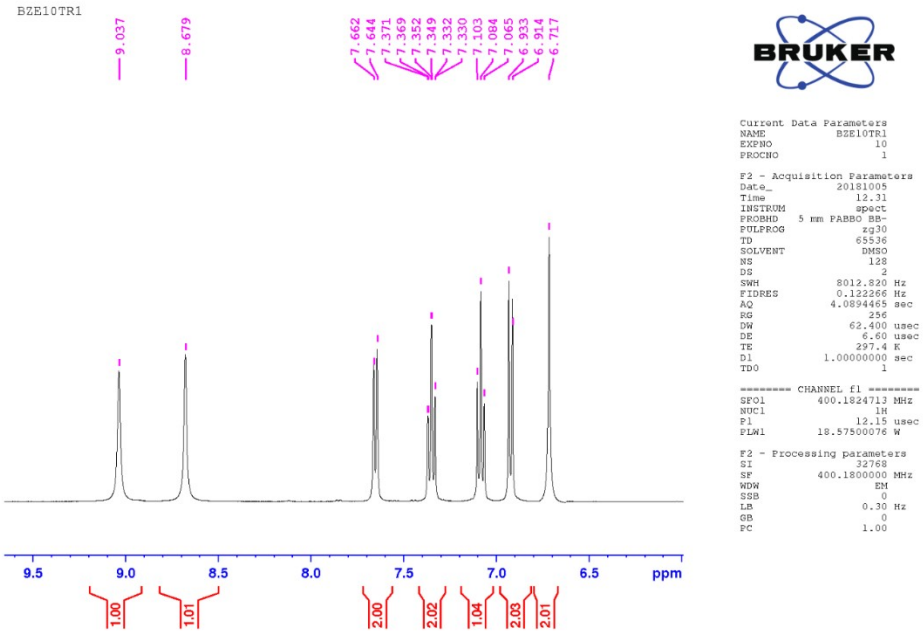


Figure S28. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8j**.

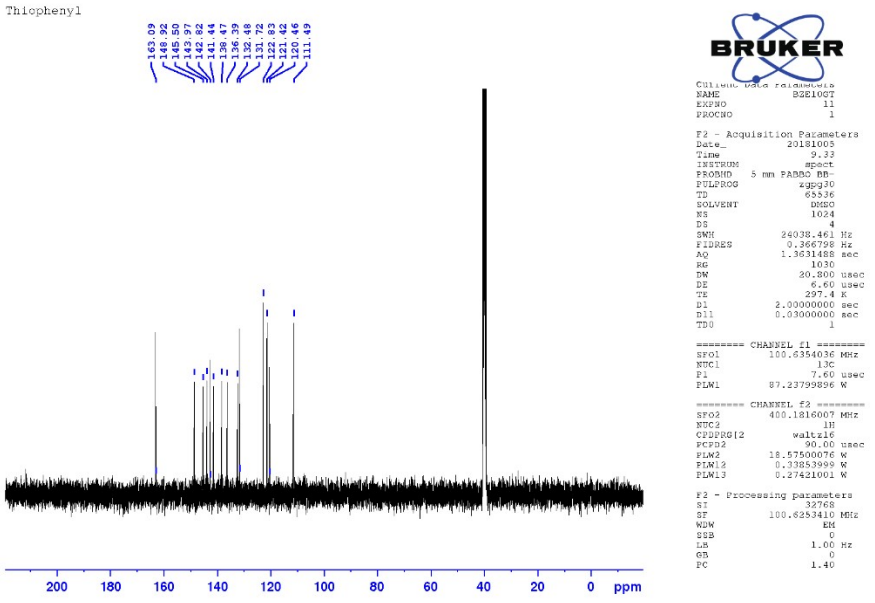
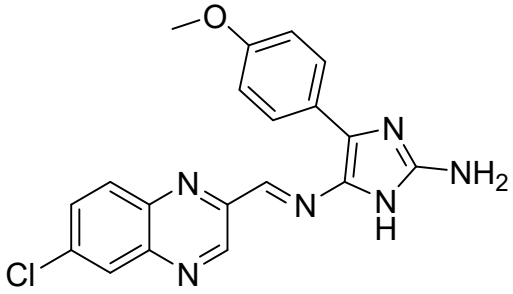


Figure S29. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8j**.

4.1.1.11. (*E*)-1-(((6-chloroquinoxalin-2-yl)methylene)amino)-4-(4-methoxyphenyl)-1*H*-imidazol-2-amine (8k)

IR (KBr): 3440 and 3251 (NH str.), 3134 and 3080 (CH str.),1622, 1466, 1170, 732, 670 cm^{-1}.^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.63 (s, 1H, 3′-H), 8.26 (d, 1H, J = 2.2 Hz, 5′-H), 8.15 (d, IH, J = 8.9 Hz, 8′-H), 8.11 (s, 1H, 5-H), 7.95 (dd, 1H, $J_{7',8'}$ = 8.9 Hz and $J_{7',5'}$ = 2.2 Hz, 7′-H), 7.68 (d, 2H, J = 8.8, 2″-H and 6″-H), 6.96 (d, 2H, J = 8.8, 3″-H and 5″-H), 6.63 (s, 2H, NH_2),3.78 (s, 3H, Me). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.8 (C-4″), 150.8 (C-2), 149.2 (C-2′), 145.6 (CHN), 144.9 (C-3′),143.2 (C-4′a), 142.1 (C-6′) 140.4 (C-4), 138.8 (C-8′a), 135.4 (C-7′), 131.5 (C-8′), 128.1 (C-5′), 127.1 (C-1″), 126.1 (C-2″ and C-6″), 114.3 (C-3″ and C-5″), 100.6 (C-5),55.5 (C-Me).



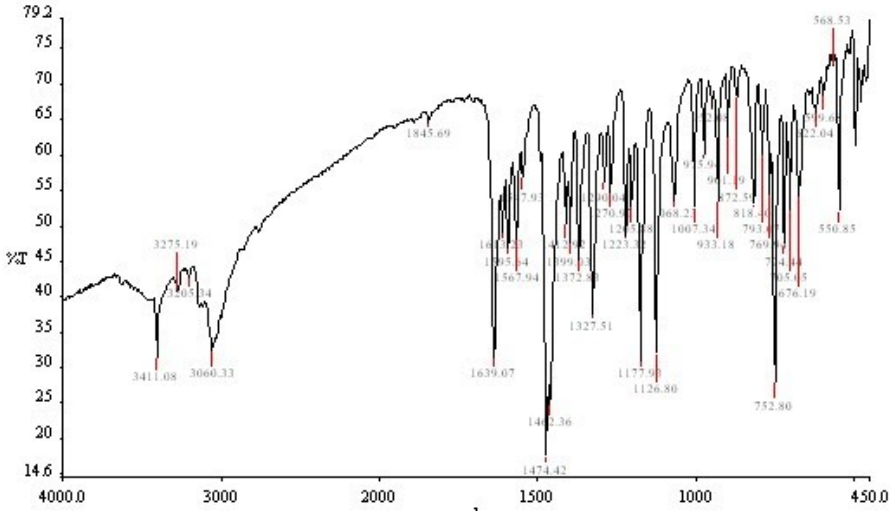


Figure S30. IR spectrum of **8k**.

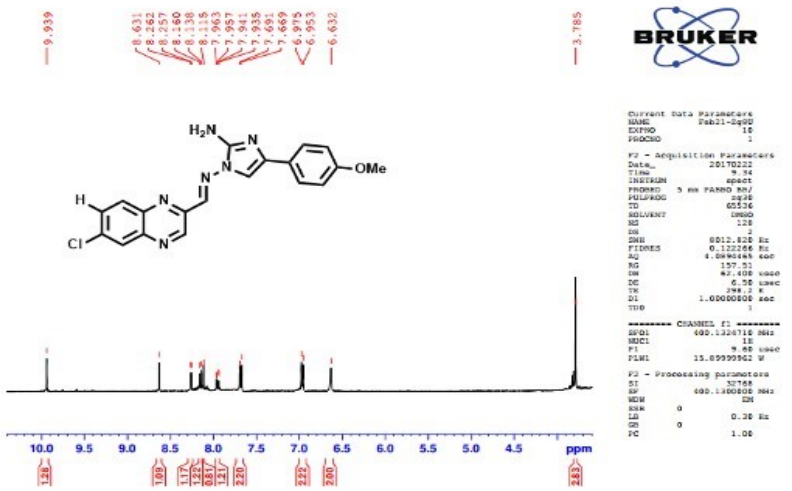


Figure S31. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8k**.

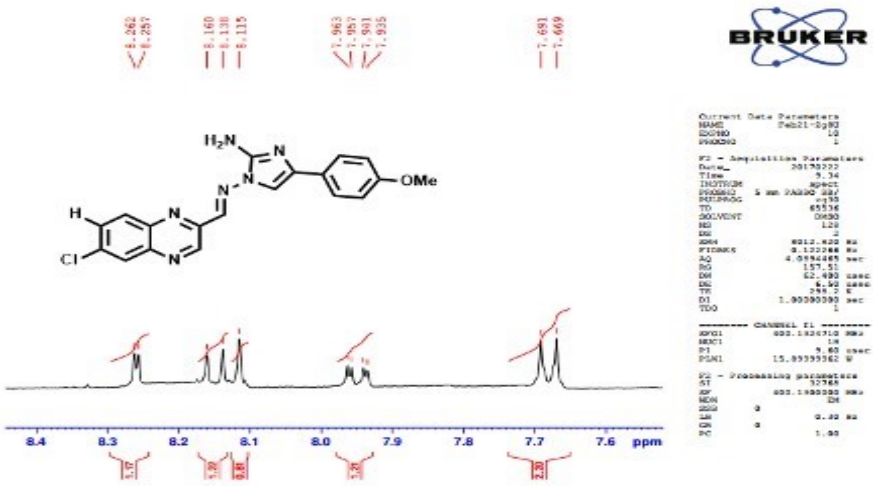


Figure S32. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8k**.

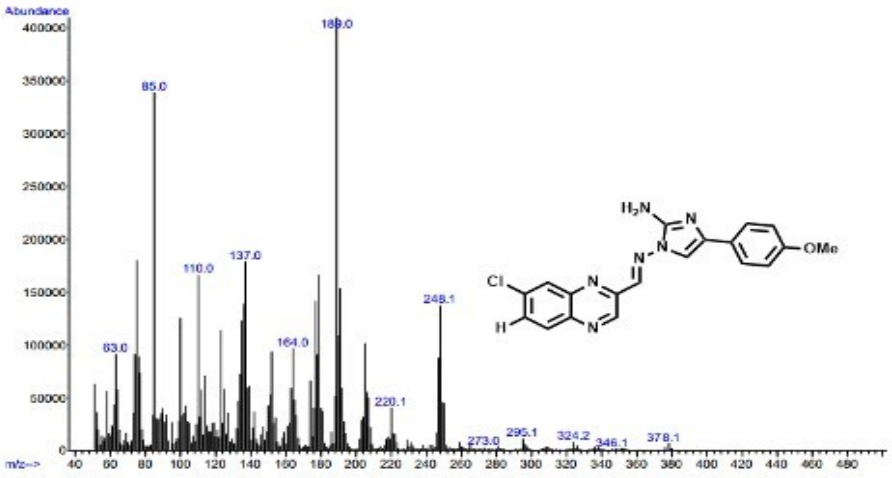


Figure S33. MAS spectrum of **8k**.

4.1.1.12. (E)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-4-phenyl-1H-imidazol-2-amine (8l)

IR (KBr): 3424 and 33302 (NH str.), 3230, 3134 and 2920 (CH str.),1642, 1466, 1171, 766, 694 cm^{-1};^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.92 (s, 1H, CHN), 8.66 (s, 1H, 3′-H), 8.25 (s, 1H, 5-H), 8.19 (d, 1H, J = 2.2 Hz, 8′-H), 8.17 (d, 1H, J = 8.8 Hz, 5′-H), 7.91 (dd, 1H, J6′,5′ = 8.8 and J6′,8′ = 2.2 Hz, 6′-H), 7.74 (d, 2H, J = 7.8 Hz, 6″-H and 2″-H), 7.36 (t, 2H, J = 7.6 Hz, 3″-H and 5″-H), 7.22 (t, 1H, J = 7.4 Hz, 4″-H),6.66 (s, 2H, NH_2);^{13}C NMR (150 MHz, DMSO-d_6) δ: 101.8 (C-5), 124.4 (C-2″ and C-6″), 126.8 (C-4″), 127.7 (C-3″ and C-5″), 128.4 (C-8′), 130.9 (C-5′), 131.2 (C-6′), 134.0 (C-1″), 135.0 (C-7′), 138.3 (C-4), 140.3 (C- 4′a), 141.7 (C-8′a), 144.5 (C-3′), 144.5 (CHN), 149.3 (C-2′), 150.5 (C-2); MS: (m/z) M^+ calcd. for $C_{18}H_{13}ClN_6$: 348.0, Found: 348.0

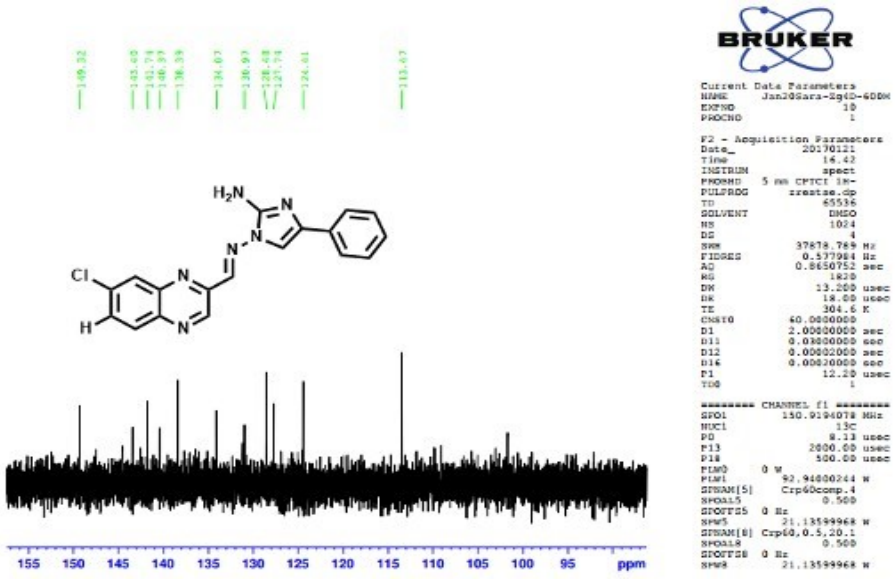


Figure S34. Expand ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8l**.

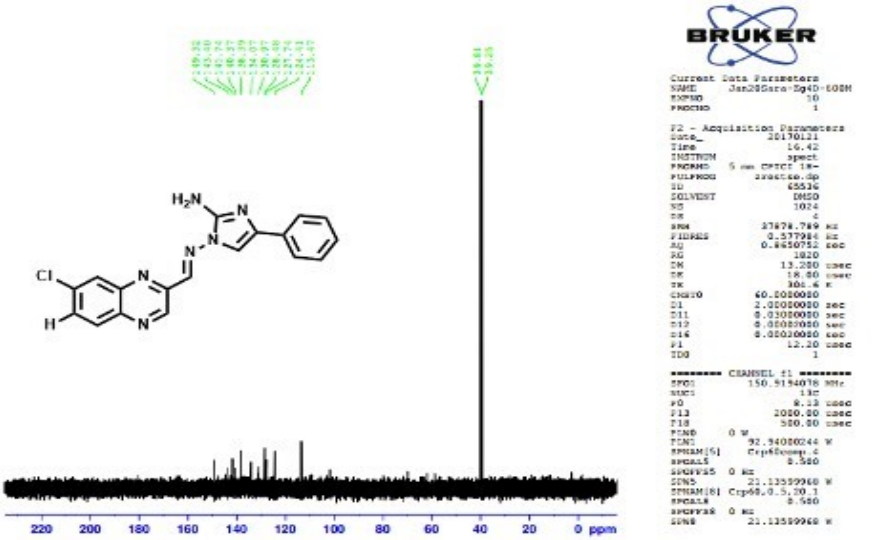


Figure S35. Expand ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8l**.

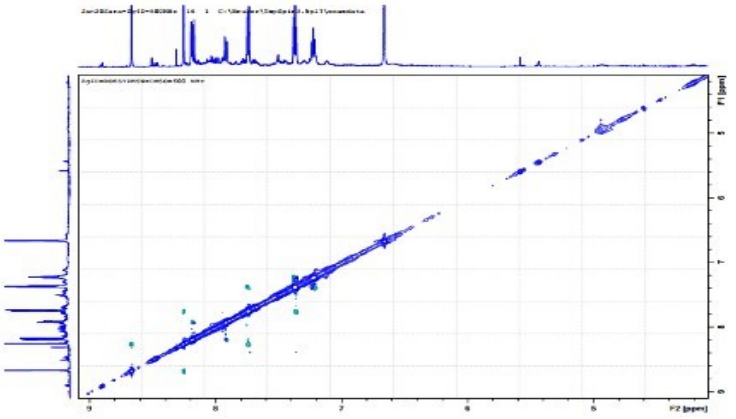


Figure S36. ROSY spectrum of **8l.**

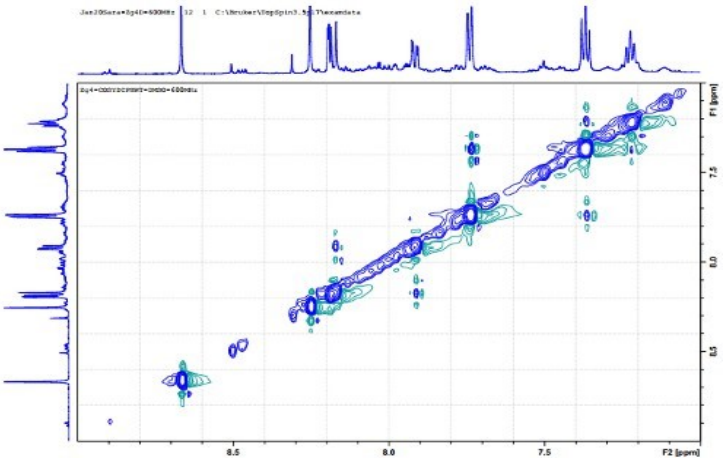


Figure S37. Expand ROSY spectrum of **8l.**

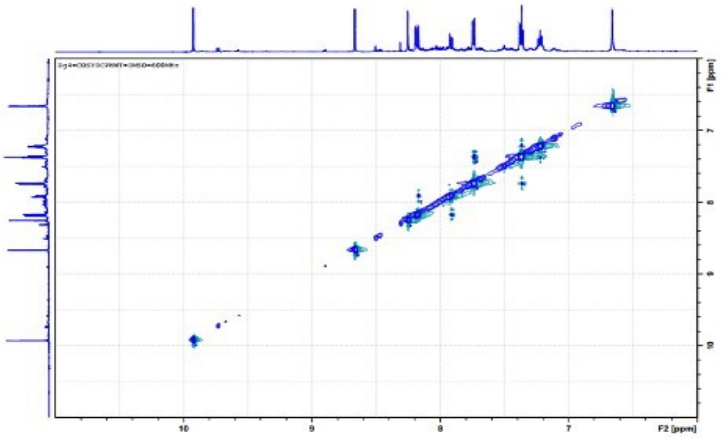


Figure S38. Expand ROSY spectrum of **8l.**

4.1.2.13. (E)-1-(((6-chloroquinoxalin-2-yl)methylene)amino)-4-(4-fluorophenyl)-1H-imidazol-2- amine (8m)

IR (KBr): 3420 and 3294 (NH str.), 3221, 3146 and 3061 (CH str.),1644, 1470, 1172, 732, 675 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.92 (s, 1H, CHN), 8.64 (s, 1H, 3′-H), 8.24 (d, 1H, J = 2.2 Hz, 5′-H), 8.15 (d, 1H, J = 8.6 Hz, 8′-H), 8.23 (s, 1H, 5-H), 7.95 (dd, 1H, $J_{7',8'}$ = 8.6 and $J_{7',5'}$ = 2.2 Hz, 7′-H), 7.74 (ab quartet, 2H, J_{HH} = 8.5 Hz, J_{HF} = 5.6, 6″-H and 2″-H), 7.20 (ab quartet, 2H, J_{HH} = 8.6 Hz, J_{HF} = 8.6 Hz, 3″-H and 5″-H),6.66 (s, 2H, NH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 161.7 C-4″), 160.4 (C-1″), 150.4 (C-2′), 148.4 (C-2), 145.0 (CH=N), 143.6 (C-3′), 141.7 (C-4′a), 139.8 (C-8′a), 137.2 (C-4), 134.9 (C-6′), 131.8 (C-7′), 130.7 (C-8′), 127.9 (C-5′), 125.8 (C-2″ and C-6″), 115.0 (C-3″ and C-5″),101.3 (C-5); MS: (m/z) M^+ calcd. for $C_{18}H_{12}ClFN_6$: 366.0, Found: 366.1

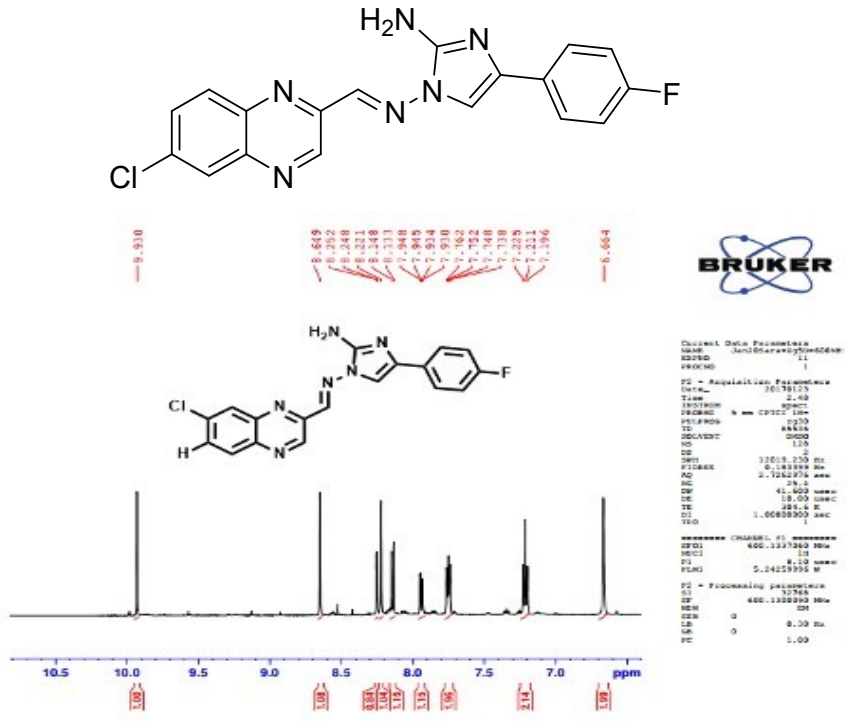


Figure S39. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8m**.

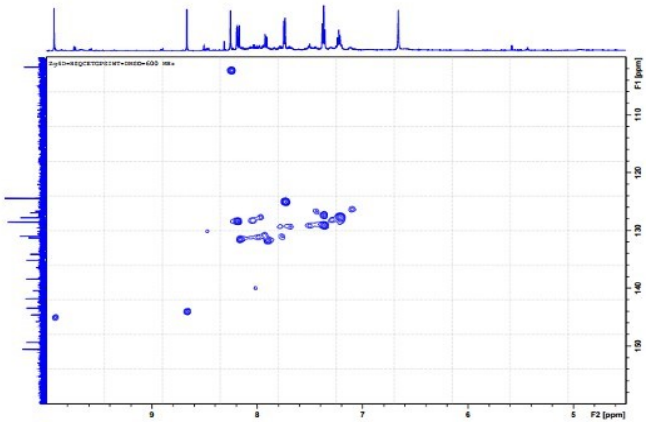


Figure S40. Expand HMBC spectrum of **8m**.

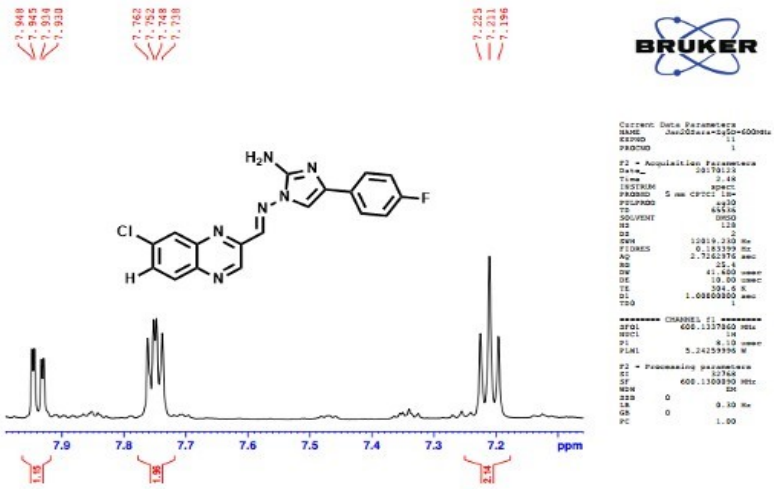


Figure S41. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8m**.

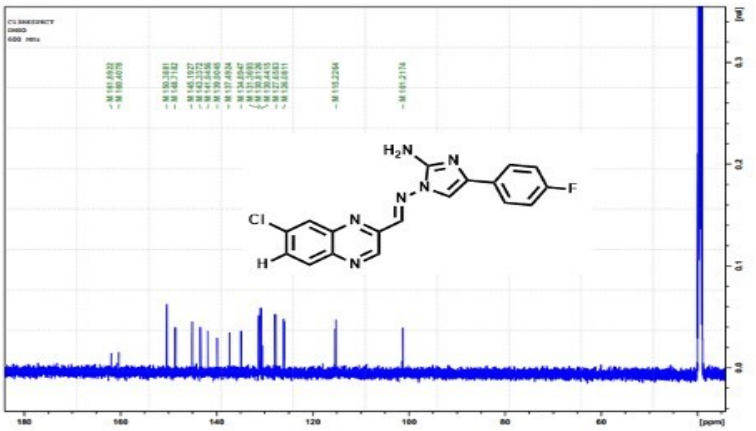


Figure S42. Expand ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8m**.

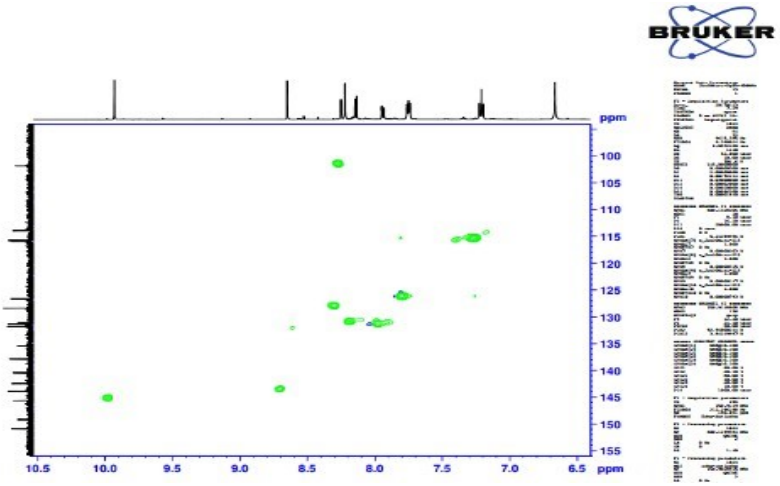


Figure S43. Expand HMBC spectrum of **8m**.

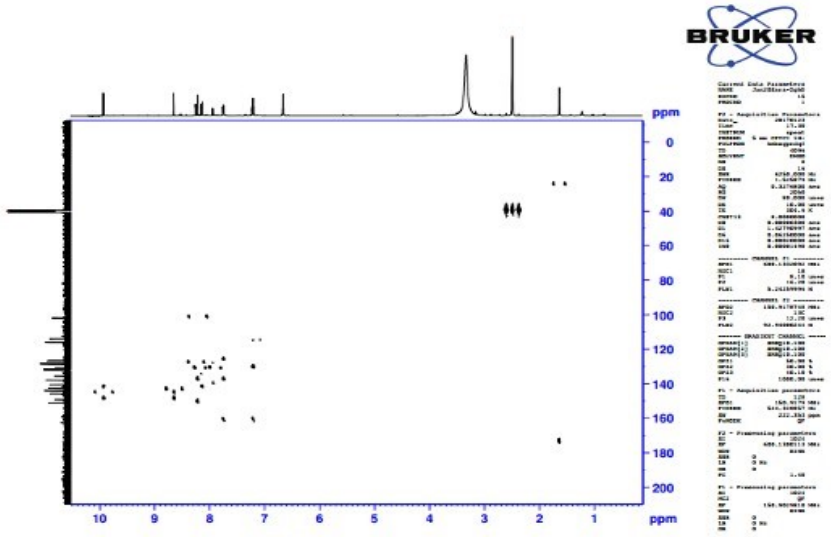


Figure S44. HMBC spectrum of **8m.**

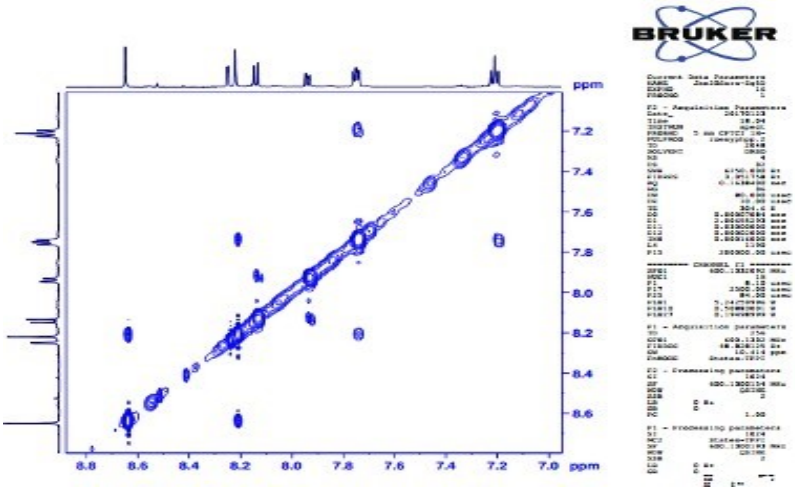


Figure S45. ROSY spectrum of **8m.**

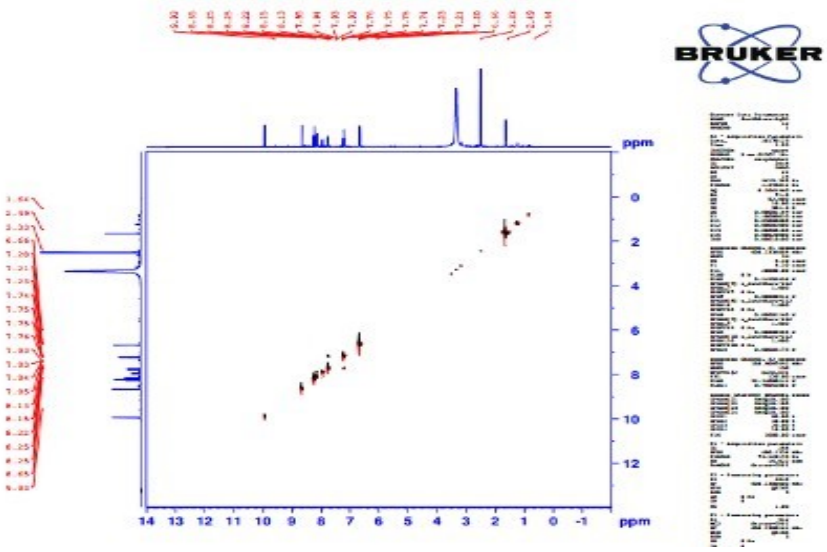


Figure S46. HH COSY spectrum of **8m.**

4.1.2.14. (E)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-4-(4-fluorophenyl)-1H-imidazol-2-amine (8n)

IR (KBr): 3420 and 3284 (NH str.), 3222, 3146 and 3062 (CH str.), 1648, 1472, 1170, 735, 676 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.65 (s, 1H, 3′-H), 8.26 (d, 1H, J = 2.2 Hz, 8′-H), 8.23 (s, 1H, 5-H), 8.15 (d, 1H, J = 8.8 Hz, 5′-H), 7.95 (dd, 1H, J6′,5′ = 8.8 and J6′,8′ = 2.2 Hz, 6′-H), 7.76 (ab quartet, 2H, JHH = 8.4 Hz, JHF = 5.7 Hz, 2″-H and 6″-H), 7.22 (ab quartet, 2H, JHH = 8.8 Hz, JHF = 8.8 Hz 3″-H and 5″-H),6.66 (s, 2H, NH_2); ^{13}C NMR (150

MHz, DMSO-d_6) δ: 161.8 (C- 4″), 160.4 (C-1″), 150.3 (C-2′), 148.7 (C-7′), 145.2 (CH=N), 143.3 (C-3′), 141.9 (C-8′a), 139.9 (C-4′a), 137.4 (C-4), 134.8 (C-7′), 131.3 (C-6′), 130.8 (C-5′), 127.6 (C-8′), 126.0 (C-2″ and C-6″), 115.2 (C-3″ and C-5″),101.8 (C-5); MS: (m/z) M+ calcd. for $C_{18}H_{12}ClFN_6$: 366.0, Found: 366.1

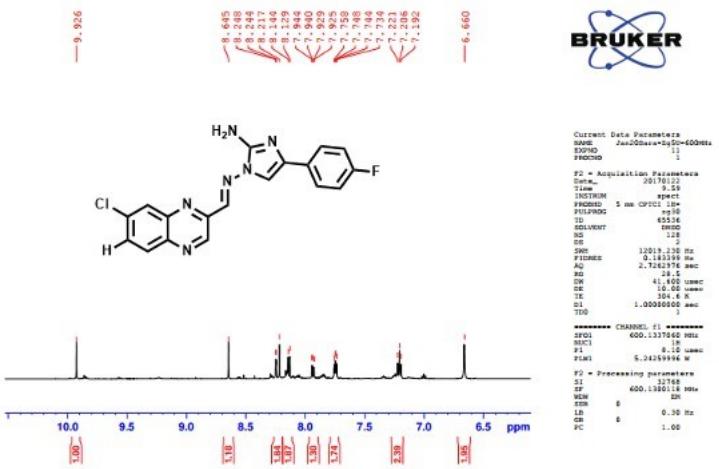


Figure S47. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8n.**

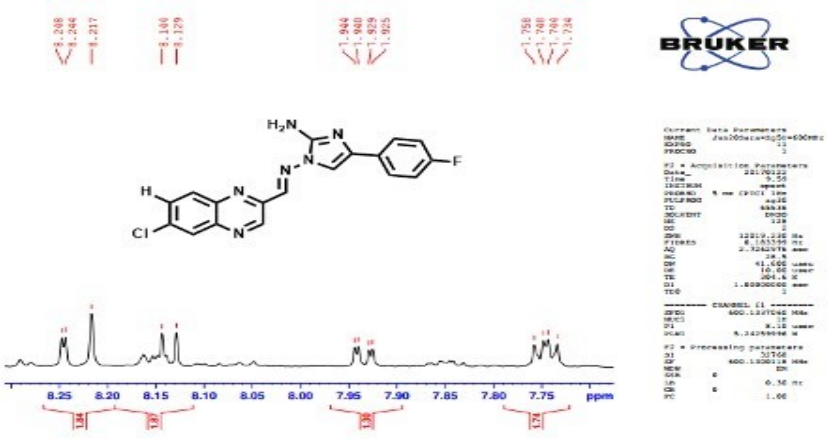


Figure S48. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8n.**

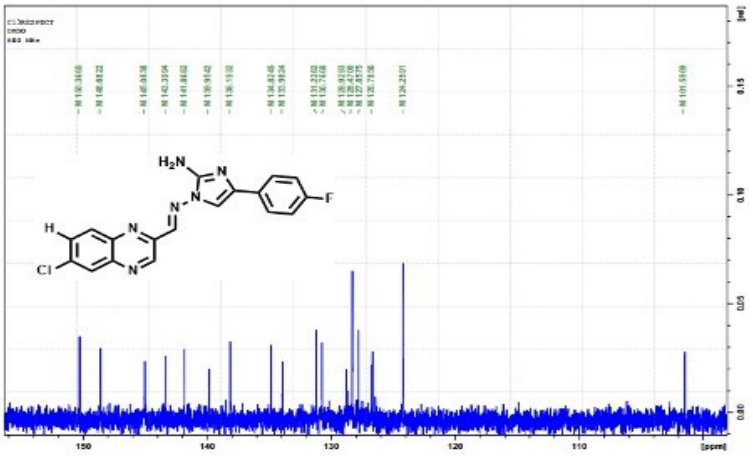


Figure S49. Expand ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8n.**

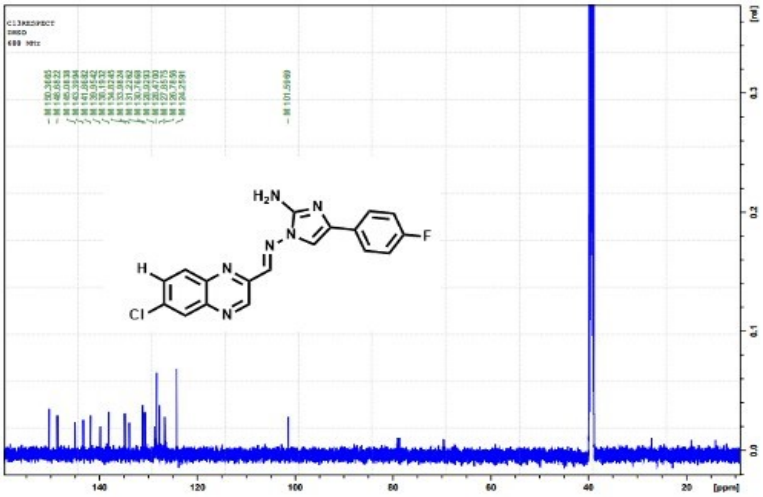


Figure S50. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8n.**

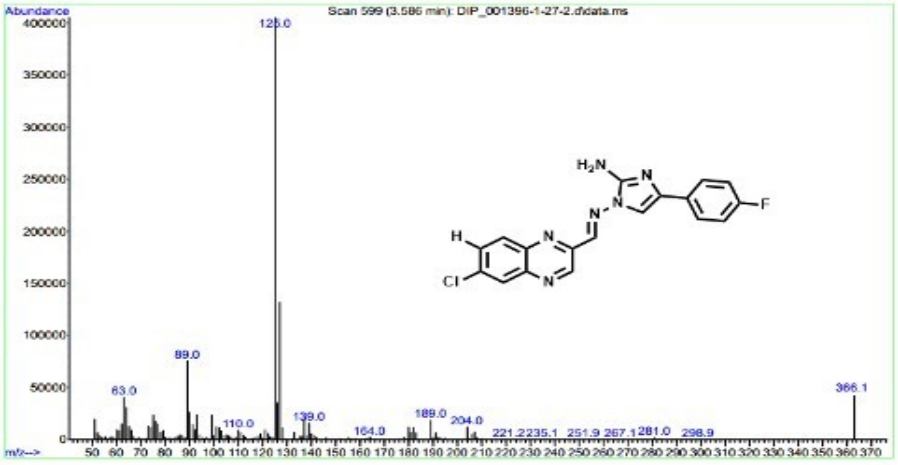


Figure S51. Mas spectrum of **8n.**

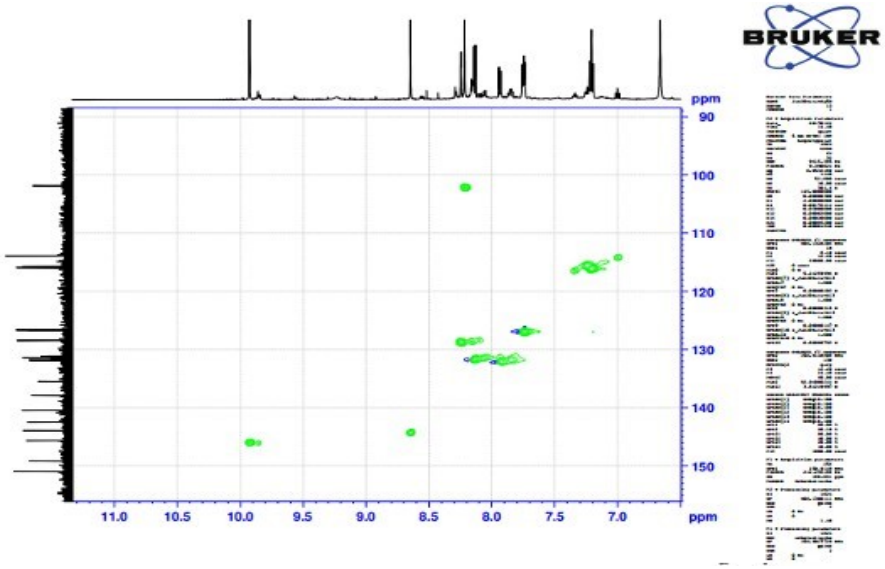
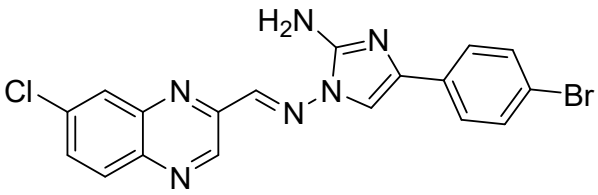


Figure S52. HMBC spectrum of **8n.**

4.1.2.15. (E)-4-(4-bromophenyl)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-1H-imidazol-2-amine (8p)

IR (KBr): 3412 and 3317 (NH str.), 3212, 3135 and 3061 (CH str.), 1638, 1472, 1177, 725, 678 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.66 (s, 1H, 3′-H), 8.33 (s, 1H, 5-H) 8.19 (d, 1H, J = 2.4, 8′-H), 8.16 (d, 1H, 5′-H, J = 8.4 Hz), 7.92 (dd, 1H, J6′,5′ = 8.6, J6′,8′ = 2.4 Hz, 6′-H), 7.58 (d, 2H, J = 8.4 Hz, 2″-H, 6″-H), 7.55 (d, 2H, J = 8.4 Hz, 3″-H and 5″-H),6.70 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 102.6 (C-5), 119.9 (C-4″), 128.1 (C-8′), 126.7 (C-

2″ and C-6″), 131.3 (C-5′), 131.8 (C-3″ and C-5″), 132.6 (C-7′), 133.8 (C-1″), 135.5 (C-6′), 137.6 (C-4), 140.4 (C-4′a), 142.1 (C-8′a), 144.2 (C-3′), 145.6 (CHN), 149.1 (C-2′), 150.9 (C-2); MS: (m/z) M+ calcd. for $C_{18}H_{12}$ $BrClN_6$: 426.0, Found: 426.0



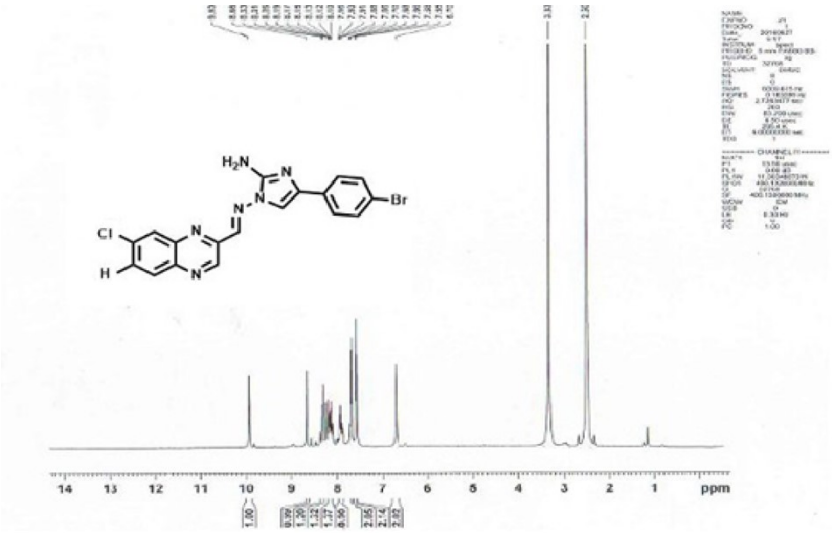


Figure S53. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of**8p.**

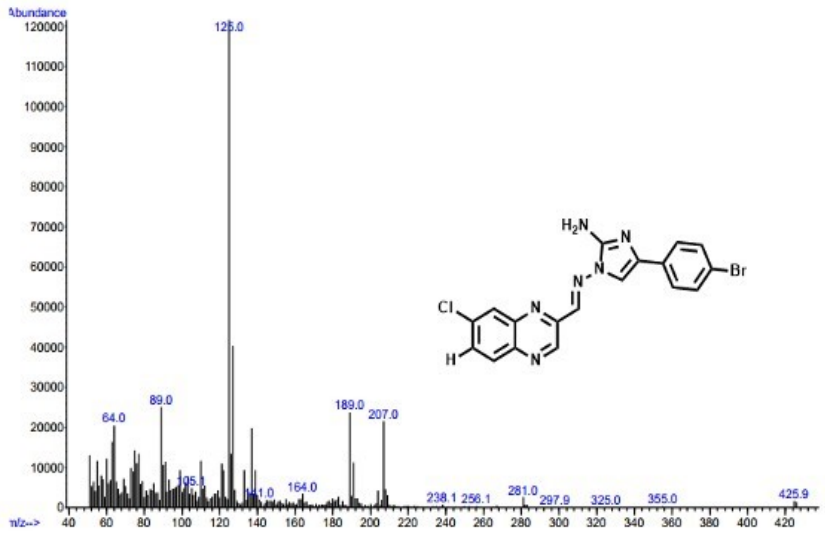
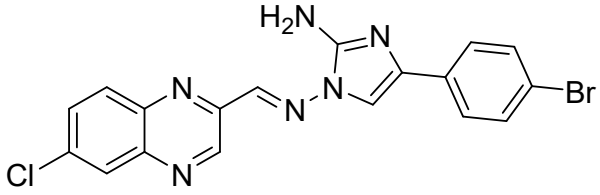


Figure S54. Mas spectrum of **8p.**

4.1.2.16. (E)-4-(4-bromophenyl)-1-(((6-chloroquinoxalin-2-yl)methylene)amino)-1H-imidazol-2-amine (8o)

IR (KBr): 3414 and 3310 (NH str.), 3214, 3132 and 3066 (CH str.), 1635, 1472, 1174, 726, 676 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.66 (s, 1H, 3′-H), 8.31 (s, 1H, 5-H), 8.25 (d, 1H, J = 2.4, 5′-H), 8.14 (d, 1H, 8′-H, J = 8.6 Hz), 7.94 (dd, 1H, $J_{7'-8'}$ = 8.6, $J_{7'-5'}$ = 2.4, 7′-H), 7.58 (d, 2H, J = 8.4 Hz, 2″-H, 6″-H), 7.55 (d, 2H, J = 8.4 Hz, 3″-H and 5″-H), 6.70 (s, 2H, NH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 150.9 (C-2), 149.1 (C-2′), 145.6 (CHN), 144.2 (C-3′),142.4 (C-4′a),140.4 (C-8′a), 137.6 (C-4), 135.5 (C-6′),133.4 (C-1″), 131.8 (C- 7′),131.4 (C-4″), 131.3 (C-8′), 129.3 (C-5′), 128.9 (C-3″ and C-5″) 126.4 (C-2″ and C-6″),102.6 (C-5), ,;MS: (m/z) M^+ calcd. for $C_{18}H_{12}BrClN_6$: 426.0, Found: 426.0



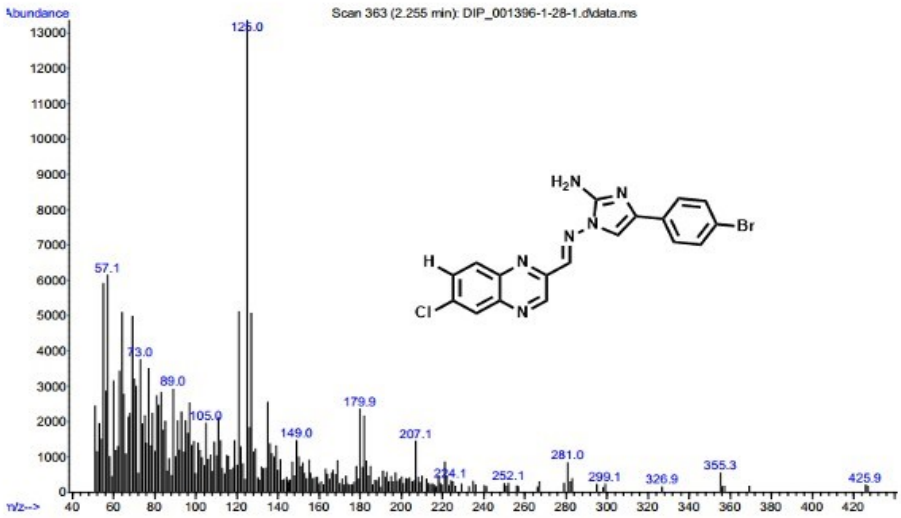


Figure S55. Mas spectrum of **8o.**

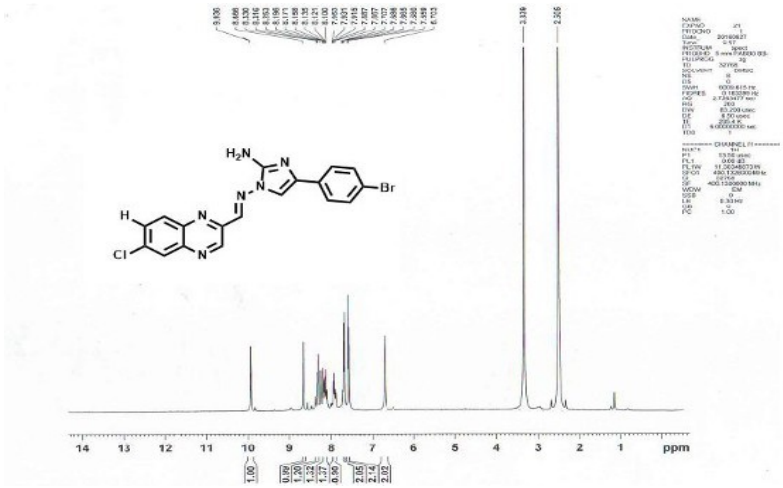


Figure S56. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8o.**

4.1.2.17. (E)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-4-(naphthalen-2-yl)-1H imidazol-2-amine (8r)

IR (KBr): 3398 and 3294 (NH str.), 3218, 3134 and 3050 (CH str.), 1625, 1468, 1168, 745, 672 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.96 (s, 1H, CHN), 8.72 (s, 1H, 3′-H), 8.26 (S, 1H, 1″-H), 8.22 (d, 1H, J = 3.36 Hz, 8′-H), 8.20 (d, 1H, J = 13.38 Hz, 5′-H), 7.96 (dd, 1H, H-6′, J6′,5′ = 13.38, J6′,8′ = 3.36 Hz, H-6′), 7.86−7.94 (m, 4H, H-3″, H-4″, H-5″, H-8″), 7.44−7.56 (m, 2H, H-

6″, H-7″),6.73 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 151.0 (C-2), 149.4 (C-2′), 146.7 (CHN), 143.3 (C-3′), 141.7 (C-8′a), 139.9 (C-4′a), 138.7 (C-4), 135.4 (C-7′), 133.7 (C-1″), 132.0 (C-6′), 131.4 (C-5′), 128.4 (C-8′), 128.3 (C-5″ and C-8″), 128.0 (C-4″), 126.7 (C-7″), 126.0 (C-6″), 123.8 (C-1″), 122.8 (C-3″),103.1 (C-5),; MS: (m/z) M^+ calcd. for $C_{22}H_{16}ClN_6$: 398.1, Found: 398.

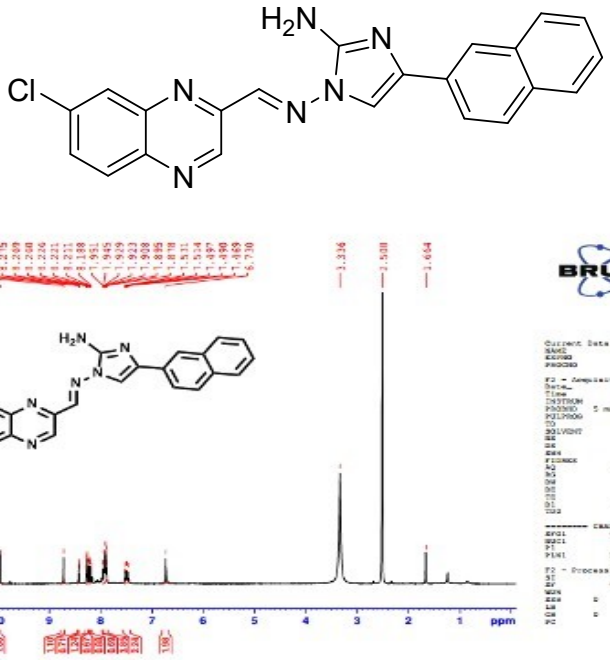


Figure S57. Expand ^1H NMR spectrum (400 MHz, DMSO-d_6) of **8r.**

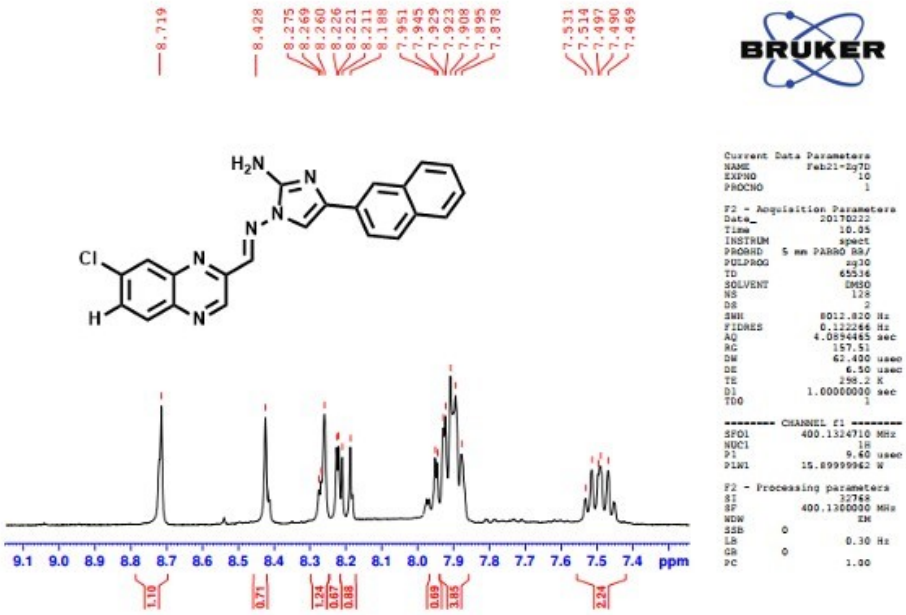


Figure S58. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8r.**

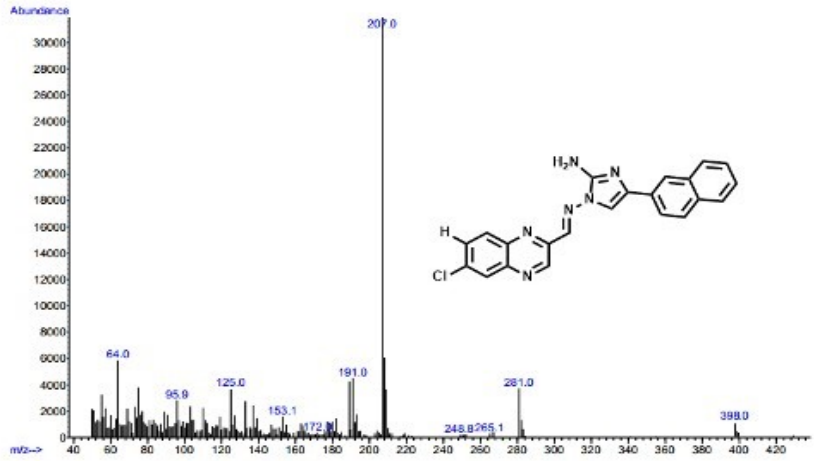


Figure S59. Mas spectrum of **8r.**

4.1.2.18. (E)-1-(((6-chloroquinoxalin-2-yl)methylene)amino)-4-(naphthalen-2-yl)-1H-imidazol-2-amine (8q)

IR (KBr): 3394 and 3296 (NH str.), 3218, 3134 and 3052 (CH str.), 1628, 1466, 1168, 745, 671 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.97 (s, 1H, CHN), 8.72 (s, 1H, 3′-H), 8.41 (s, 1H, 5-H),

8.27 (d, 1H, J = 3.42 Hz, 5′-H), 8.25 (s, 1H, 1″-H), 8.17 (d, 1H, J = 13.44 Hz, 8′-H), 7.96 (dd, 1H, $J_{7',8'}$ = 13.44, $J_{7',5'}$ = 3.42 Hz, H-7′), 7.85−7.94 (m, 4H, H-3″, H-4″, H-5″, H-8″), 7.43−7.55 (m, 2H, H-6″, H-7″),6.72 (s, 2H, NH_2);^{13}C NMR (100 MHz, DMSO-d_6) δ: 151.0 (C- 2), 149.4 (C-2′), 146.7 (CHN), 143.3 (C-3′), 141.7 (C-4′a), 139.9 (C-8′a), 138.7 (C-4), 135.4 (C-6′), 132.0 (C-7′),133.7 (C-1″), 131.4 (C-8′), 128.4 (C-5′), 128.3 (C-5″ and C-8″), 128.0 (C- 4″), 126.7 (C-7″), 126.0 (C-6″), 123.8 (C-1″), 122.8 (C-3″),103.1 (C-5); MS: (m/z) M^+ calcd. for $C_{22}H_{16}ClN_6$: 398.1, Found: 398.0

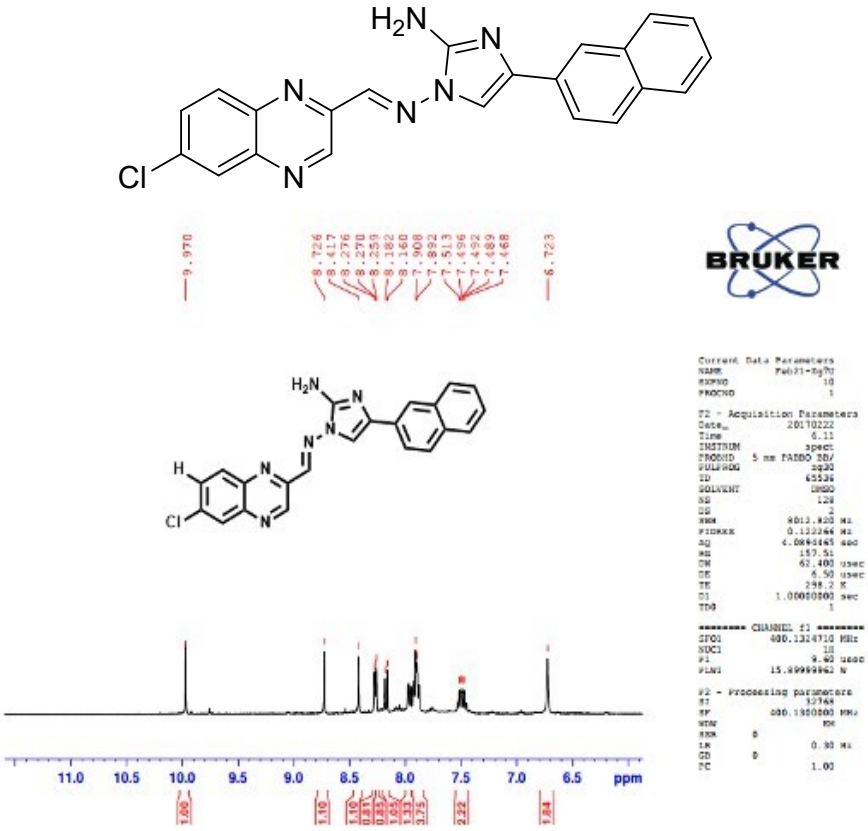


Figure S60. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8q.**

Figure S61. Mas spectrum of **8q.**

4.1.2.19. (E)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-4-(4-methoxyphenyl)-1H-imidazol- 2-amine (8t)

IR (KBr): 3434 and 3250 (NH str.), 3136 and 3082 (CH str.), 1626, 1463, 1170, 736, 670 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.62 (s, 1H, 3′-H), 8.19 (s, 1H, 5-H), 8.08 (d, 1H, J = 2.3 Hz, 8′-H), 7.97 (d, IH, J = 8.8 Hz, 5′-H), 7.92 (dd, 1H, J6′,8′ = 2.3 and J6′,5′ = 8.8 Hz, 6′-H), 7.68 (d, 2H, J = 8.8, 2″-H and 6″-H), 6.96 (d, 2H, J = 8.8, 3″-H and 5″-H), 6.62 (s, 2H, NH_2),3.78 (s, 3H, Me);^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.8 (C-4″), 150.8 (C-2), 149.2 (C-2′), 144.9 (C-3′), 143.2 (C-8′a), 145.6 (CHN), 142.3 (C-7′), 140.4 (C-4), 135.4(C-6′),138.8 (C-4′a), 131.7 (C-5′), 128.3 (C-8′), 127.1 (C-1″), 126.1 (C-2″ and C-6″), 114.3 (C-3″ and C-5″), 100.6 (C- 5),55.5 (C-Me); MS: (m/z) M^+ calcd. for $C_{19}H_{15}ClN_6O$: 378.1, Found: 378.0

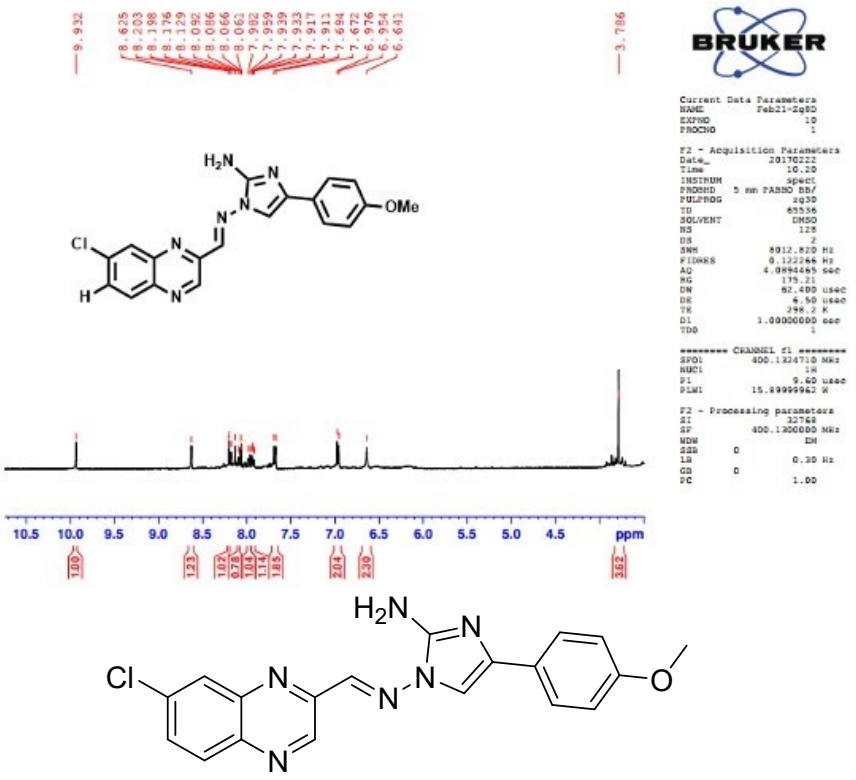


Figure S62. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8t.**

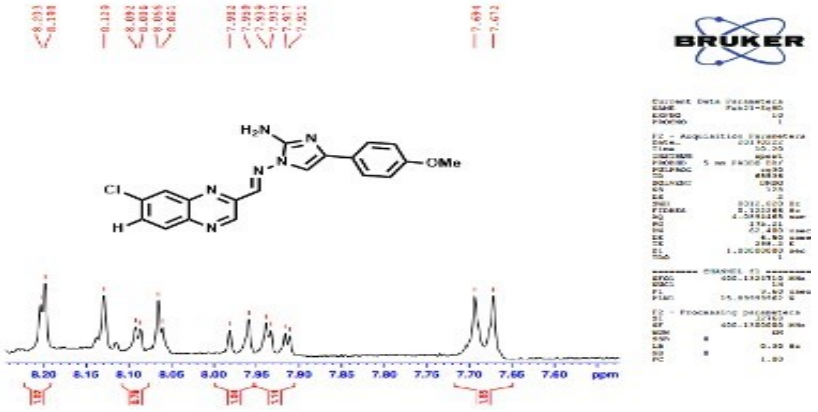


Figure S63. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8t.**

Figure S64. Mas spectrum of **8t.**

4.1.2.20.(E)-1-(((6-chloroquinoxalin-2-yl)methylene)amino)-4-(4-methoxyphenyl)-1H-imidazol-2- amine (8s)

IR (KBr): 3434 and 3250 (NH str.), 3136 and 3080 (CH str.),1626, 1463, 1174, 737, 676 cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.93 (s, 1H, CHN), 8.63 (s, 1H, 3′-H), 8.26 (d, 1H, J = 2.2 Hz, 5′-H), 8.15 (d, IH, J = 8.9 Hz, 8′- H), 8.11 (s, 1H, 5-H), 7.95 (dd, 1H, $J_{7',8'}$ = 8.9 Hz and $J_{7',5'}$ = 2.2 Hz, 7′-H), 7.68 (d, 2H, J = 8.8, 2″-H and 6″-H), 6.96 (d, 2H, J = 8.8, 3″-H and 5″-H), 6.63 (s, 2H, NH_2),3.78 (s, 3H, Me);^{13}C NMR (150 MHz, DMSO-d6) δ: 158.8 (C-4″), 150.8 (C-2), 149.2 (C-2′), 145.6 (CHN), 144.9 (C-3′),143.2 (C- 4′a), 142.1 (C-6′), 140.4 (C-4), 138.8 (C-8′a), 135.4 (C-7′), 131.5 (C-8′), 128.1 (C-5′), 127.1 (C- 1″), 126.1 (C-2″ and C-6″), 114.3 (C-3″ and C-5″),100.6 (C-5), 55.5 (C-Me); MS: (m/z) M^+ calcd. For $C_{19}H_{15}ClN_6O$: 378.1, Found: 378.0

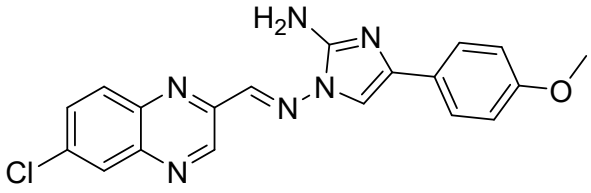


Figure S65. Mas spectrum of **8s.**

Figure S66. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **8s**.

Figure S67. Expand ^{1}HNMR spectrum (100 MHz, DMSO-d_6) of **8s**.

4.1.2.21. (E)-4-(4-chlorophenyl)-1-(((7-chloroquinoxalin-2-yl)methylene)amino)-1H-imidazol-2-amine (8v)

IR (KBr): 3434 and 3302 (NH str.), 3226, 3138 and 3034 (CH str.), 1662, 1468, 1174, 828, 729 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.94 (s, 1H, CHN), δ: 8.67 (s, 1H, 3′-H), δ: 8.32 (s, 1H, 5-H), 8.21 (d, 1H, J = 3.42 Hz, 8′-H), 8.19 (d, 1H, J = 13.38 Hz, 5′-H), 7.93 (dd, 1H, J6′,5′ = 13.38, J6′,8′ = 3.42 Hz, 6′-H), 7.75 (d, 2H, J = 12.76 Hz, 2″- H, 6″-H), 7.44 (d, 2H, J = 12.76 Hz, 3″-H and 5″-H), 6.71 (S, 2H, NH_2); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 150.9 (C-2), 149.1 (C-2′), 145.6 (CHN), 144.2 (C-3′),142.4 (C-8′a), 140.4 (C-4′a), 137.6 (C-4), 135.5 (C-7′),133.4 (C-1″), 131.8 (C-6′),131.4 (C-4″), 131.3 (C-5′), 130.7 (C-8′), 128.9 (C-3″ and C-5″), 126.4 (C-2″ and C-6″),102.6 (C-5),; MS: (m/z) M+ calcd. for $C_{18}H_{12}Cl_2N_6$: 382.0, Found: 382.1

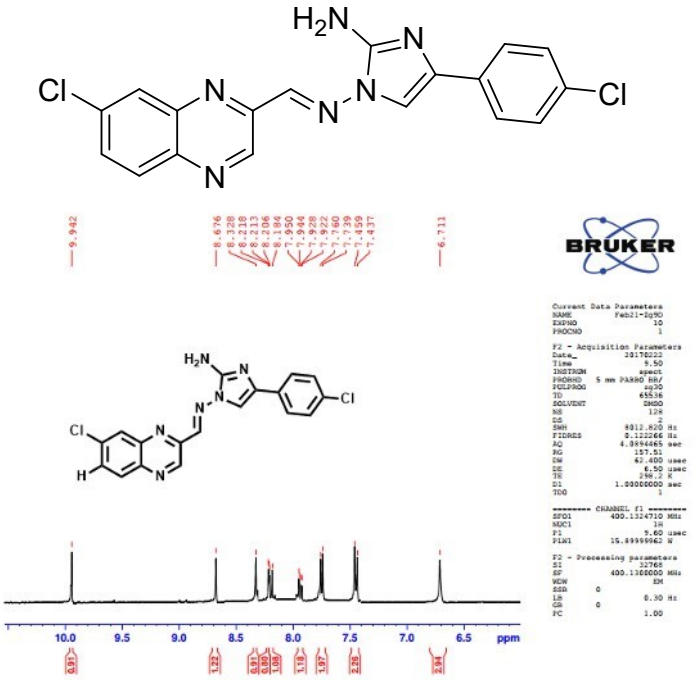


Figure S68. Expand ^{1}HNMR spectrum (100 MHz, DMSO-d_6) of **8v.**

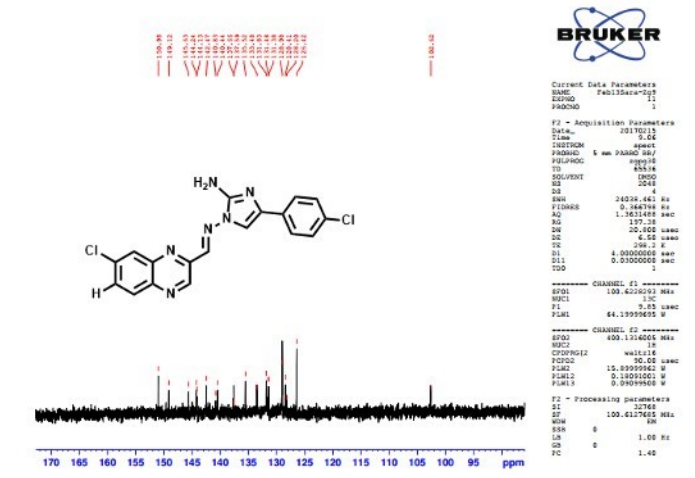


Figure S69. Expand ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of **8v**.

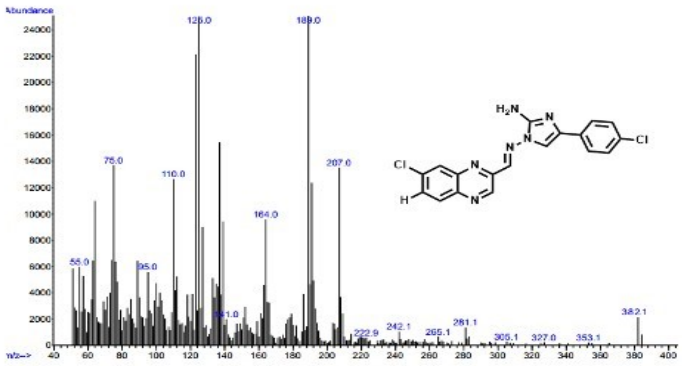


Figure S70. Mas spectrum (100 MHz, DMSO-d_6) of **8v.**

Figure S71. Expand ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **8v.**

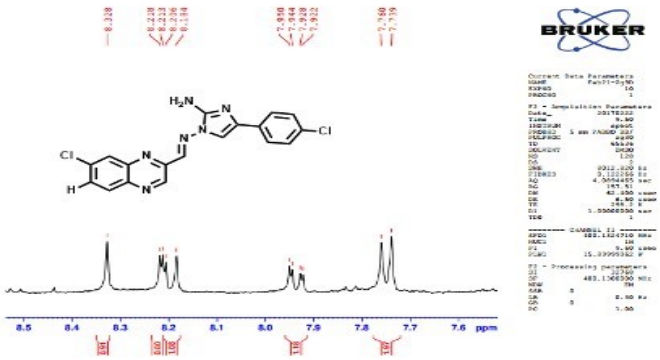
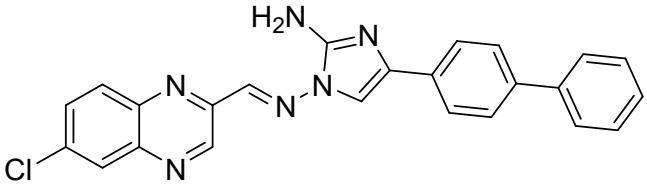


Figure S72. Expand ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of **8v.**

4.1.2.22. (E)-4-([1,1'-biphenyl]-4-yl)-1-(((6-chloroquinoxalin-2-yl)methylene)amino) 1Himidazol- 2-amine (4w*)*

IR (KBr): 3404 and 3276 (NH str.), 3204, 3064 and 2920 (CH str.), 1639, 1442, 1171, 736, 698 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6) δ: 9.93 (s, 1H, CHN), 8.68 (s, 1H, 3′-H), 8.32 (s, 1H, 5-H), 8.24 (d, 1H, J= 2.4 Hz, 5′-H), 8.14(d, 1H, J = 8.8 Hz, 8′-H), 7.93 (dd, 1H, J7′,8′ = 8.8 and J7′,5′ = 2.4 Hz, 7′-H), 7.83 (d, 2H, J = 8.4 Hz, 2″-H and 6″- H), 7.67-7.73 (m, 4H, 3″-H, 5″-H, H-2 phenyl and H-6 phenyl), 7.46 (t, 2H, J = 7.4 Hz, H-3 phenyl and H-5 phenyl), 7.35 (t, 1H, J = 7.4 Hz, H-4 phenyl),6.69 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d6) δ: 150.9 (C-2), 149.1 (C-2′), 145.6 (CHN), 143.9 (C-3′), 142.4 (C-6′) 140.4 (C-8′a), 140.2 (C-4′a), 138.7 (C-4), 138.4 (C-4″), 135.4 (C-1 phenyl), 133.6 (C-1″), 131.3 (C-7′), 129.6 (C-8′), 129.3 (C-3 and C-5 phenyl), 128.3 (C-5′), 127.7 (C-4 phenyl), 127.1 (C-2″ and C-6″), 126.8 (C-2 and C-6 phenyl), 125.3 (C-3″ and C-5″),102.3 (C-5); MS: (m/z) M+ calcd. For $C_{24}H_{17}ClN_6$: 424.1, Found: 424.0



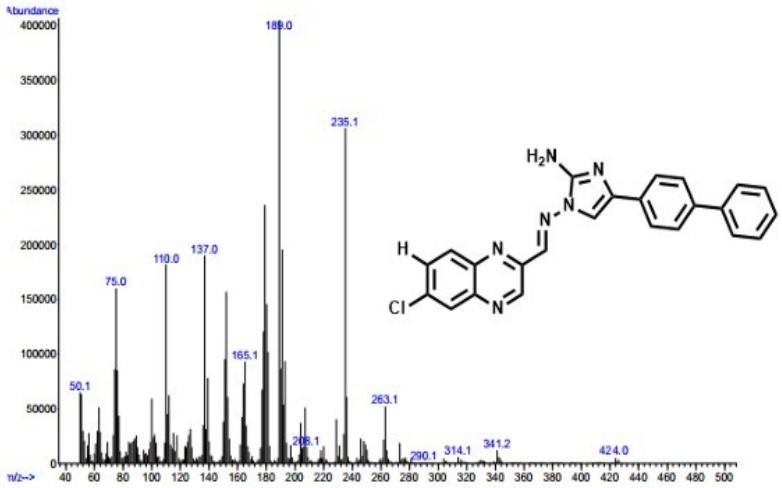


Figure S73. Mas spectrum of **4w.**

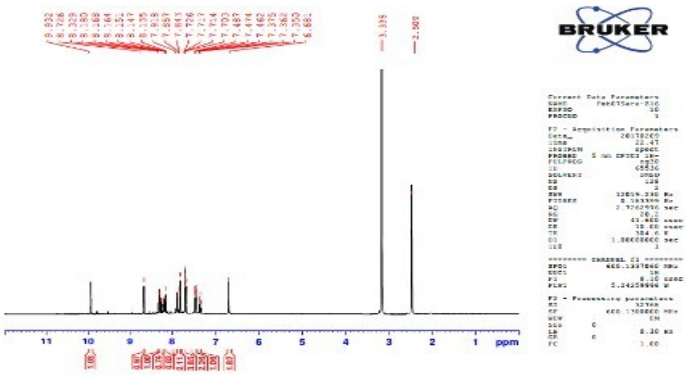


Figure S74. Expand ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **4w**.