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First synthesis of allyl isonitriles from Baylis-Hillman adducts and their synthetic application for obtaining substituted imidazo[1,2-a]pyridine and dibenzoazulene systems

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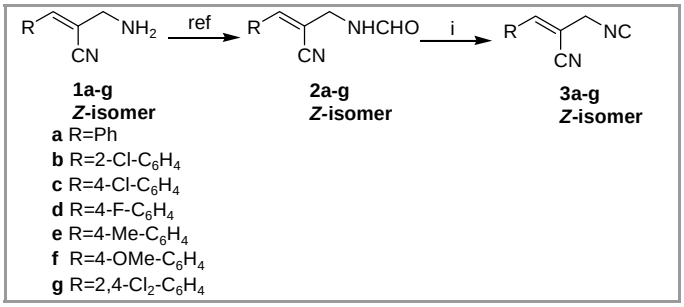
Abstract: First report of stereoselective synthesis of substituted allyl isonitriles from the primary allyl amines generated from the Baylis-Hillman adduct and its utilization in a robust IMCR to afford substituted imidazo[1,2-a]pyridine in the presence of NH_4Cl is described.

Key words: Isonitrile, Baylis-Hillman, allyl amine, MCR, imidazo[2,1-a]pyridine

The development of novel synthetic intermediates which lead to the formation of multiple-ring containing heterocyclic systems is progressive feature of synthetic organic chemistry. The Baylis-Hillman reaction is considered to be a complexity generating C-C bond forming reaction. Perhaps the three chemospecific functional group present in the product of this reaction makes them attractive option for achieving the synthesis of an array of diverse molecular frameworks.[1] Not only these products but the derivatives furnished from them have also been innovatively employed for developing facile and general approaches for the generation of novel compounds including the aforementioned heterocycles. One such useful intermediate which can be readily and stereoselectively synthesized from the Baylis-Hillman adduct is the substituted primary allyl amine.[2] Such allyl amines have been demonstrated by us to be viable precursors for several nitro-containing heterocyclic systems.[3] In our recent report[1] we have proposed that the N-formyl derivatives which could be readily synthesized by the reaction of primary allyl amine and formamide[3b] may be utilized for the synthesis of substituted isonitriles which in turn may serve as one of the reactants in several of the well established isonitrile-based multicomponent reactions (IMCR).[4] We have now been able to optimize the preparation of these substituted isonitriles and have used them as one of the reactant in the IMCR to afford the substituted imidazo[1,2-a]pyridine. Further the substituted imidazopyridine have been used as substrate for obtaining novel dibenzoazulene system. The detail of this work is being presented in this communication.

The allyl amines **1a-g** were stereoselectively prepared following the reported strategy.[2] Compounds **1a-g** on reaction with formamide at 120 ^oC for 2 h resulted in the required formamides **2a-g**. Treatment of **2a-g** with phosphorous oxychloride in the presence of triethylamine at low temperature gave the desired isonitriles **3a-g** in 55-70% yields (scheme-1). Stereochemistry of allyl isonitriles was maintained as *Z*. Strikingly the molecular ion peak in the mass spectra of isonitriles, except for **3g** which was a trimer, were observed to be tetramer (Fig. 1). These isonitriles were odourless and were stable at room temperature.



Scheme 1 Reagent and conditions: i) $POCl_3$, Et_3N, THF, -20^oC to 0^oC, 2 h

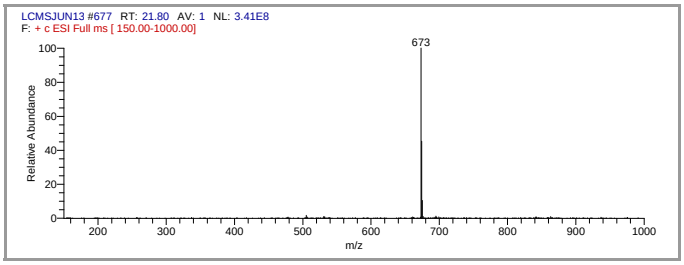
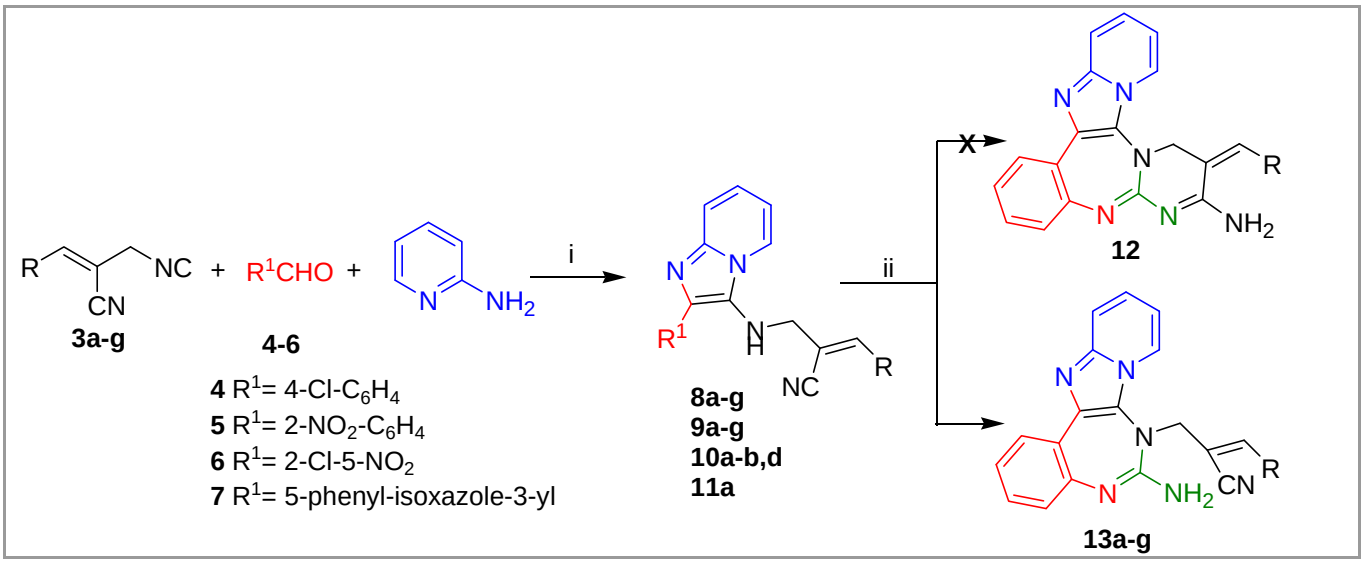


Figure 1 The ES mass spectrum of **3a**

One of the most common IMCR involves the reaction between isonitrile, 2-aminopyridine and an aldehyde for affording substituted imidazo[2,1-a]pyridine core.[5] Compounds comprising of this scaffold have been ascribed with a variety of pharmacological properties.[6] These include anticancer, anticoccidial, antigastric, antiviral, antithrombotic and antiprotozoal. In order to demonstrate the synthetic potential of the isonitriles synthesized during the present study, reaction of **3a-g** with 2-aminopyrdine and different aryl aldehydes **(4-7)** were performed in the presence of ammonium chloride[5b] as shown in scheme 2. It was pleasing to note that all isonitriles participated in the MCR to yield the substituted imidazo[1,2-a]pyridines **(8-9a-g, 10a-b,d, 11a)** in moderate to good yields.

We have been interested for the synthesis of heterocyclic scaffolds which incorporates the guanidine subunit in the cyclic framework.[1a,3c] Consequently it was envisaged



Scheme 2. Reagents and conditions: i) NH_4Cl, Toluene, 110°C, 5-6 h; ii) a) In-HCl, THF: H_2O (1:1, v/v), rt, 1 h; b) BrCN, K_2CO_3, rt, 9 h.

that reduction of the nitro-group in **9** followed by reaction with cyanogen bromide may trigger concomitant intramolecular cyclizations to yield **12**. Accordingly as part of optimization, compound **9a** was treated with In-HCl under aqueous condition. The reaction was complete within 1 h. but the purification of the amine via column chromatography was unsuccessful. Therefore the crude amine was treated with cyanogen bromide in the presence of K_2CO_3 in THF at room temperature. The reaction was complete in 9 h and the work up of the reaction mixture led to the product which was purified via silica-gel-based column chromatography to obtain the pure compound in 66% yield. The spectroscopic analysis however established the structure of the product as **13a** instead of the expected **12**. As in the case of **9a**, all other substrates **9b-g** were initially reduced in the presence of In-HCl and then reacted with cyanogen bromide to provide **13b-g** in 65-75% yields. In the next stage we attempted the intramolecular cyclization between the amino and the nitrile group in the presence of different bases but were unsuccessful.

In summary we have disclosed the first successful stereoselective synthesis of allyl isonitriles from the Baylis-Hillman adducts and have demonstrated their participation in IMCR to afford substituted imidazo[2,1-a]pyridines. These imidazo[2,1-a]pyridine were further utilized for the synthesis of dibenzoazulene system. Further work to explore the synthetic utility of substituted isonitriles synthesized herein is underway in our laboratory.

Melting points are uncorrected and were determined in capillary tubes on an apparatus containing silicon oil. IR spectra were recorded using a Perkin Elmer's Spectrum RX I FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded either on a Bruker DPX-200 FT or Bruker Avance DRX-300 spectrometer, using TMS as an internal standard (chemical shifts in δ). The ESMS were recorded on MICROMASS Quadro-II LCMS system. The HRMS spectra were recorded as EI-HRMS on a JEOL system. Elemental analyses were performed on a Carlo Erba's 108 or an Elementar's Vario EL *III* microanalyzer. Due to poor solubility of the compounds **13a-g** even in DMSO-d_6 the ^{13}C NMR spectra could not be recorded.

General procedure for the synthesis of Isonitriles (3a-g) as exemplified for 3a:

Triethyl amine (7.9 ml, 56.6 mmol) was added to a stirred solution of **2a** (0.5g, 2.27 mmol) in THF (8.0 mL) and the mixture was cooled to -10 °C in ice salt bath. Then a solution of $POCl_3$ (1.07 mL, 11.35 mmol) in THF (5.0 mL) was added drop wise to the reaction mixture at same temperature. The reaction mixture was allowed to reach 0 °C and continued for another 2 h. Thereafter the mixture was cooled to -20 °C and quenched by drop wise addition of water (20 mL), followed by further addition of 100mL of water and extracted with diethyl ether (50 mL). The aqueous phase was extracted with diethyl ether (2 × 40 ml), the organic layers were combined, dried over anhyd. Na_2SO_4 and concentrated in vacuo to afford the crude product. Purification by column chromatography on silica gel using EtOAc: hexanes (25: 75, v/v) as the eluent led to pure 0.3 g (65%) of **3a** as a yellow solid.

(*Z*)-2-(Isocyanomethyl)-3-phenylprop-2-enenitrile (3a)

Yield: 61% as yellow oil; R_f= 0.42 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (Neat) 2150 (NC), 2218 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.37 (s, 2H, CH_2), 7.30 (s, 1H, =C*H*), 7.41-7.49 (m, 3H, ArH), 7.78-7.81 (m, 2H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 45.1, 102.5, 116.2, 129.1, 129.2, 129.3, 131.6, 146.2, 161.5

mass (ES+) *m/z*= 673 $[4M+1]^+$

(*Z*)-3-(2-Chlorophenyl)-2-(isocyanomethyl)prop-2-enenitrile (3b)

Yield: 60% as a yellow solid, mp 72-73 ^oC; R_f= 0.54 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2152 (NC), 2219 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.41 (s, 2H, CH_2), 7.38-7.43 (m, 2H, ArH), 7.47-7.50 (m, 1H, ArH), 7.70 (s, 1H, =CH), 7.98 (dd, 1H, J_1= 2.3 Hz, J_2= 6.6 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 45.0, 106.1, 115.6, 127.6, 129.4, 130.3, 130.6, 132.5, 134.8, 143.0, 162.2

mass (ES-) *m/z*= 807 $[4M-1]^-$, 201 $[M-1]^-$

(*Z*)-3-(4-Chlorophenyl)-2-(isocyanomethyl) prop-2-enenitrile (3c)

Yield: 65% as a yellow solid, mp 75-76 ^oC; R_f= 0.28 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2152 (NC), 2220 (CN) cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ= 4.38 (s, 2H, CH_2), 7.26 (s, merged with $CDCl_3$, 1H, =C*H*), 7.45 (d, 2H, *J*= 8.6 Hz, ArH), 7.75 (d, 2H, *J*= 8.5 Hz, ArH)

^{13}C NMR (50 MHz, $CDCl_3$) δ= 45.0, 103.0, 116.0, 129.6, 130.5, 137.7, 144.6, 162.0

mass (ES-) *m/z*= 807 $[4M-1]^-$, 201 $[M-1]^-$

(*Z*)-3-(4-Fluorophenyl)-2-(isocyanomethyl)prop-2-enenitrile (3d)

Yield: 70% as a yellow solid, mp 79-80 ^oC; R_f= 0.42 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2152 (NC), 2220 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.37 (s, 2H, CH_2), 7.17 (t, 2H, *J*= 8.6 Hz, ArH), 7.26 (s, merged with $CDCl_3$, 1H, =CH), 7.81 (d, 1H, *J*= 5.3 Hz, ArH), 7.83 (d, 1H, *J*= 5.3 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 45.1, 102.2, 116.5, 116.7, 128.4, 131.6, 131.7, 144.9, 161.8, 166.2

mass (ES+) *m/z*= 745 $[4M+1]^+$

(*Z*)-2-(Isocyanomethyl)-3-(4-methylphenyl)prop-2-enenitrile (3e)

Yield: **5**6% as a brown solid, mp 61-62 ^oC; R_f= 0.46 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2151 (NC), 2213 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 2.43 (s, 3H, CH_3), 4.37 (s, 2H, CH_2), 7.28-7.30 (m, 3H, ArH and =CH), 7.72 (d, 2H, *J*= 8.0 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 21.8, 45.3, 101.2, 116.6, 127.6, 128.5, 129.5, 130.1, 146.3

mass (ES+) *m/z*= 729 $[4M+1]^+$

(*Z*)-2-(Isocyanomethyl)-3-(4-methoxyphenyl)prop-2-enenitrile (3f)

Yield: 62% as a yellow solid, mp 71-72 ^oC; R_f= 0.35 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2151 (NC), 2217 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.87 (s, 3H, OCH_3), 4.33 (s, 2H, CH_2), 6.97 (dd, 2H, J_1= 2.0 Hz, J_2= 6.9 Hz, ArH), 7.19 (s, 1H, =CH), 7.79 (d, 2H, *J*= 8.8 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 45.4, 55.7, 99.2, 114.7, 115.0, 116.9, 124.8, 131.4, 131.5, 146.0, 148.9, 162.4

mass (ES+) *m/z*= 793 $[4M+1]^+$

(*Z*)-3-(2,4-Dichlorophenyl)-2-(isocyanomethyl)prop-2-enenitrile (3g)

Yiled: 46% as a yellow solid, mp 80-81 ^oC; R_f= 0.58 (hexanes: EtOAc, 80: 20, v/v)

ν_{max} (KBr) 2152 (NC), 2224 (CN) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.42 (s, 2H, CH_2), 7.39 (d, 1H, *J*= 8.4 Hz, ArH), 7.51 (s, 1H, =CH), 7.64 (s, 1H, ArH), 7.94 (d, 1H, *J*= 8.4 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 44.9, 106.6, 115.3, 128.1, 129.1, 130.1, 130.2, 135.6, 138.0, 141.7, 162.5

mass (ES-) *m/z*= 707 $[3M-1]^-$

General procedure for the synthesis of compounds (8a-g), (9a-g), (10a-b, 10d) and 11a:

A solution of 2-amino pyridine (0.094 g, 1.0 mmol) and an appropriate aldehyde from **4-7** (1.0 mmol) in toluene (15 mL) was heated for 30 min. Solid NH_4Cl (0.107 g, 2.0 mmol) and an appropriate isonitrile from **3a-g** (1.0 mmol) were added and the reaction mixture was brought to reflux. After 5-6 h, 100 mL of water was added and the mixture was extracted with EtOAc (3 x 30 mL). The organic layers were pooled, dried over anhyd. Na_2SO_4 and concentrated in vacuo. The residue so obtained was purified via silica gel-based column chromatography using 30-50 % EtOAc: hexanes (30-50: 70-50, v/v) as the eluent to afford pure products in 50-65 % yields.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-phenylprop-2-enenitrile (8a)

Yield: 54% as a yellow solid, mp 155-156 ^oC; R_f= 0.20 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2206 (CN), 3418 (NH) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ= 3.59 (t, 1H, *J*= 6.0 Hz, CH_2NH), 3.93 (d, 2H, *J*= 5.5 Hz, CH_2NH), 6.77 (s, 1H, =CH), 6.91 (dt, 1H, J_1=1.7 Hz, J_2= 10.2 Hz, ArH), 7.15-7.23 (m, 1H, ArH), 7.36-7.46 (m, 5H, ArH), 7.52-7.58 (m, 3H, ArH), 7.95 (dd, 2H, J_1=2.0 Hz, J_2= 6.7 Hz, ArH), 8.29 (d, 1H, *J*= 6.9 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.1, 108.9, 112.4, 117.6, 118.6, 122.6, 123.6, 124.9, 128.5, 128.7, 128.8, 128.89, 128.93, 129.0, 130.8, 132.6, 132.8, 133.6, 136.7, 142.0, 145.4

mass (ES+) *m/z*= 385.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{17}ClN_4$: 384.1142. Found: 384.1142.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(2-chlorophenyl)prop-2-enenitrile (8b)

Yield: 58% as a yellow solid, mp 119-120 ^{o}C; R_f= 0.22 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2208 (CN), 3417 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.49 (t, 1H, *J*= 5.9 Hz, CH_2NH), 3.83 (d, 2H, *J*= 5.9 Hz, CH_2NH), 6.90 (dt, 1H, J_1= 1.0 Hz, J_2= 6.8 Hz, ArH), 7.15 (s, 1H,=*CH*), 7.19-7.25 (m, 1H, ArH), 7.29-7.39 (m, 3H, ArH), 7.53-7.57 (m, 2H, ArH), 7.62 (dd, 1H, J_1= 1.3 Hz, J_2= 7.6 Hz, ArH)-7.68 (dt, 1H, J_1= 1.9 Hz, J_2= 6.8 Hz, ArH), 7.76 (dd, 1H, J_1= 1.4 Hz, J_2= 7.7 Hz, ArH), 7.95 (dd, 1H, J_1= 1.1 Hz, J_2= 8.0 Hz, ArH), 8.26 (d, 1H, *J*= 6.9 Hz, ArH)

^{13}C NMR (50 MHz, $CDCl_3$) δ= 52.9, 110.0, 112.7, 118.0, 122.9, 123.7, 125.3, 127.5, 128.9, 129.4, 129.5, 130.1, 131.6, 131.8, 132.9, 134.0, 134.5, 142.3

mass (ES+) *m/z*= 419.1 [M+1]$^+$

Anal. Calcd. for $C_{23}H_{16}Cl_2N_4$; C, 65.88; H, 3.85; N, 13.36. Found C, 65.66; H, 4.08; N, 13.12.

***Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-chlorophenyl)prop-2-enenitrile (8c)**

Yield: 68% as a yellow solid, mp 171-172 ^{o}C; R_f= 0.22 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2216 (CN), 3422 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.64 (s, 1H, CH_2NH), 3.91 (d, 2H, *J*= 5.8 Hz, CH_2NH), 6.68 (s, 1H, =CH), 6.87 (t, 1H, *J*= 6.8 Hz, ArH), 7.16-7.22 (m, 1H, ArH), 7.33 (d, 2H, *J*= 8.6 Hz, ArH), 7.41-7.48 (m, 4H, ArH), 7.53-7.56 (m, 1H, ArH), 7.93 (d, 2H, *J*= 8.6 Hz, ArH), 8.25-8.27 (m, 1H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.1, 109.6, 112.6, 117.7, 118.5, 122.7, 123.6, 125.2, 128.6, 129.1, 129.3, 130.2, 131.3, 132.6, 133.8, 136.8, 136.9, 142.2, 144.0

mass (ES+) *m/z*= 419.1 [M+1]$^+$

Anal. Calcd. for $C_{23}H_{16}Cl_2N_4$; C, 65.88; H, 3.85; N, 13.36. Found C, 65.95; H, 3.77; N, 13.21.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-fluorophenyl)prop-2-enenitrile (8d)

Yield: 61% as a yellow solid, mp 136-137 ^{o}C; R_f= 0.35 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2209 (CN), 3342 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.61 (t, 1H, *J*= 5.7 Hz, CH_2NH), 3.91 (d, 2H, *J*= 5.8 Hz, CH_2NH), 6.68 (s, 1H, =CH), 6.86 (t, 1H, *J*= 6.7 Hz, ArH), 7.05 (t, 2H, *J*= 8.5 Hz, ArH), 7.19 (t, 1H, *J*= 7.8 Hz, ArH), 7.42 (d, 2H, *J*= 8.4 Hz, ArH), 7.54 (dd, 3H, J_1= 3.3 Hz, J_2= 6.7 Hz, ArH), 7.93 (d, 2H, *J*= 8.4 Hz, ArH), 8.26 (d, 1H, *J*= 6.7 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.9, 108.5, 112.4, 116.0, 116.3, 117.5, 118.6, 122.6, 123.5, 125.0, 128.5, 129.0, 130.9, 131.1, 132.5, 133.6, 136.6, 142.1, 144.0, 162.2

mass (ES+) *m/z*= 403.1 [M+1]$^+$

Anal. Calcd. for $C_{23}H_{16}ClFN_4$; C, 68.57; H, 4.00; N, 13.91. Found C, 68.55; H, 4.09; N, 13.75.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-methylphenyl)prop-2-enenitrile (8e)

Yield: 51% as a yellow solid, mp 122-123 ^{o}C; R_f= 0.24 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2213 (CN), 3368 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 2.36 (s, 3H, CH_3), 3.60 (t, 1H, *J*= 5.7 Hz, CH_2NH), 3.91 (d, 2H, *J*= 5.9 Hz, CH_2NH), 6.73 (s, 1H, =CH), 6.83-6.88 (m, 1H, ArH), 7.16-7.21 (m, 3H, ArH), 7.41-7.48 (m, 4H, ArH), 7.54 (d, 1H, *J*= 9.1 Hz, ArH), 7.95 (d, 2H, *J*= 8.6 Hz, ArH), 8.28 (d, 1H, *J*= 6.9 Hz, ArH)

^{13}C NMR (50 MHz, $CDCl_3$) δ= 21.7, 53.3, 107.6, 112.5, 117.6, 119.0, 122.8, 123.8, 125.1, 128.6, 129.1, 129.14, 129.8, 130.2, 132.7, 133.8, 136.6, 141.6, 142.2, 145.6

mass (ES+) *m/z*= 399.1 [M+1]$^+$

HR-EIMS Calcd. for $C_{24}H_{19}ClN_4$: 398.1298. Found: 398.1287.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-methoxyphenyl)prop-2-enenitrile (8f)

Yield: 63% as a yellow solid, mp 165-166 ^{o}C; R_f= 0.22 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2203 (CN), 3344 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.57 (t, 1H, *J*= 6.0 Hz, CH_2NH), 3.83 (s, 3H, OCH_3), 3.88 (d, 2H, *J*= 5.6 Hz, CH_2NH), 6.67 (s, 1H, =CH), 6.82-6.90 (m, 3H, ArH), 7.14-7.20 (m, 1H, ArH), 7.40-7.44 (m, 2H, ArH), 7.52-7.57 (m, 3H, ArH), 7.94 (dd, 2H, J_1= 1.9 Hz, J_2= 6.7 Hz, ArH), 8.26-8.28 (m, 1H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.3, 55.6, 105.7, 112.5, 114.4, 117.6, 119.3, 122.8, 123.9, 125.0, 125.7, 128.6, 129.1, 130.9, 132.8, 133.7, 136.6, 142.2, 145.1, 161.7

mass (ES+) *m/z*= 415.1 [M+1]$^+$

Anal. Calcd. for $C_{24}H_{19}ClN_4O$; C, 69.48; H, 4.62; N, 13.50. Found C, 69.64; H, 4.49; N, 13.21.

(*Z*)-2-({[2-(4-Chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(2,4-dichlorophenyl)prop-2-enenitrile (8g)

Yield: 52% as a yellow solid, mp 151-152 ^{o}C; R_f= 0.20 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2205 (CN), 3380 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.69 (s, 1H, CH_2NH), 3.95 (d, 2H, *J*= 4.2 Hz, CH_2NH), 6.88 (s, 1H, ArH), 7.02 (s, 1H, =CH), 7.38-7.45 (m, 4H, ArH), 7.56 (d, 3H, *J*= 8.4 Hz, ArH), 7.95 (d, 2H, *J*= 7.5 Hz, ArH), 8.25 (d, 1H, *J*= 5.1 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.7, 112.6, 113.1, 117.8, 122.7, 123.4, 125.2, 127.8, 128.7, 129.2, 129.9, 132.6, 133.9, 135.1, 137.1, 140.9, 142.3

mass (ES+) *m/z*= 453.1 [M+1]$^+$

HR-EIMS Calcd. for $C_{23}H_{15}Cl_3N_4$: 452.0363. Found: 452.0395.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-phenylprop-2-enenitrile (9a)

Yield: 55% as a yellow solid, mp 129-131 ^oC; R_f= 0.15 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2209 (CN), 3173 (NH)cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.48 (t, 1H, *J*= 6.1 Hz, CH_2NH), 3.79 (d, 2H, *J*= 5.9 Hz, CH_2NH), 6.76 (s, 1H, =CH), 6.89 (t, 1H, *J*= 6.6 Hz, ArH), 7.20 (t, 1H, *J*= 7.4 Hz, ArH), 7.34-7.37 (m, 3H, ArH), 7.46-7.62 (m, 5H, ArH), 7.68-7.71 (m, 1H, ArH), 7.89 (d, 1H, *J*= 7.2 Hz, ArH), 8.25 (d, 1H, *J*= 6.9 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.1, 108.8, 112.6, 118.0 118.3, 122.7, 124.4, 124.8, 124.9, 128.8, 128.9, 129.0, 130.7, 132.58, 132.64, 132.9, 134.5, 142.2, 145.3, 149.5

mass (ES+) *m/z*= 396.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{17}N_5O_2$: 395.1382. Found: 395.1346.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(2-chlorophenyl)prop-2-enenitrile (9b)

Yield: 51% as a yellow solid, mp 122-123 ^oC; R_f= 0.25 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2216 (CN), 3348 (NH) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 3.65 (t, 1H, *J*= 5.9 Hz, CH_2NH), 3.99 (d, 2H, *J*= 5.9 Hz, CH_2NH), 6.89 (t, 1H, *J*= 6.3 Hz, ArH), 7.16 (s, 1H, =CH), 7.22 (dt, 1H, J_1= 1.1 Hz, J_2= 7.9 Hz ArH), 7.30-7.34 (m, 2H, ArH), 7.36-7.40 (m, 1H, ArH), 7.47 (d, 2H, *J*= 8.6 Hz, ArH), 7.58 (d, 1H, *J*= 9.0 Hz, ArH), 7.66-7.69 (m, 1H, ArH), 7.99 (d, 2H, *J*= 8.6 Hz, ArH), 8.29 (d, 1H, *J*= 6.8 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 51.8, 111.8, 112.0, 116.8 117.3, 122.0, 124.1, 124.2, 126.4, 128.2, 128.3, 129.1, 130.6, 130.8, 131.9, 133.5, 133.7, 141.0, 141.5

mass (ES+) *m/z*= 430.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{16}ClN_5O_2$: 429.0993. Found: 429.0972.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-chlorophenyl)prop-2-enenitrile (9c)

Yield: 50% as yellow viscous oil; R_f= 0.20 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (Neat) 2215 (CN), 3347 (NH) cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ= 3.52 (t, 1H, *J*= 4.3 Hz, CH_2NH), 3.79 (d, 2H, *J*= 4.3 Hz, CH_2NH), 6.71 (s, 1H, =CH), 6.89 (t, 1H, *J*= 5.1 Hz, ArH), 7.43-7.48 (m, 4H, ArH), 7.62-7.69 (m, 3H, ArH), 7.84 (d, 2H, *J*= 6.4 Hz, ArH), 8.11 (d, 1H, *J*= 5.9 Hz, ArH), 8.24 (d, 1H, *J*= 5.1 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.9, 109.3, 112.7, 117.9, 122.7, 124.4, 125.0, 128.7, 128.9, 129.1, 129.6, 130.1, 131.2, 131.3, 132.5, 132.6, 134.4, 136.6, 142.2, 143.9, 149.4

mass (ES+) *m/z*= 430.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{16}ClN_5O_2$: 429.0993. Found: 429.0986.

(*Z*)-3-(4-Fluorophenyl)-2-({[2-(2-nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)prop-2-enenitrile (9d)

Yield: 45% as yellow viscous oil, R_f= 0.19 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (Neat) 2215 (CN), 3375 (NH) cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ= 3.51 (s, 1H, CH_2NH), 3.78 (d, 2H, *J*= 5.0 Hz, CH_2NH), 6.71 (s, 1H, =CH), 6.89 (d, 2H, *J*= 6.1 Hz ArH), 7.00-7.06 (m, 3H, ArH), 7.53-7.58 (m, 5H, ArH), 7.89 (d, 1H, *J*= 8.2 Hz, ArH), 8.24 (d, 1H, *J*= 6.6 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.1, 108.4, 112.8, 116.0, 116.3, 118.0, 118.4, 122.8, 124.6, 124.8, 125.2, 128.8, 129.1, 131.1, 131.2, 132.7, 132.8, 142.3, 144.2

mass (ES+) *m/z*= 414.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{16}FN_5O_2$: 413.1288. Found: 413.1289.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-methylphenyl)prop-2-enenitrile (9e)

Yield: 55% as yellow viscous oil; R_f= 0.30 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (Neat) 2212 (CN), 3385 (NH) cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ= 2.38 (s, 3H, CH_3), 3.49 (t, 1H, *J*= 5.7 Hz, CH_2NH), 3.79 (d, 2H, *J*= 5.5 Hz, CH_2NH), 6.73 (s, 1H, =CH), 6.87-6.92 (m, 1H, ArH), 7.16-7.18 (m, 2H, ArH), 7.45-7.56 (m, 5H, ArH), 7.62 (dt, 1H, J_1= 1.3 Hz, J_2= 7.5 Hz, ArH), 7.71 (dd, 1H, J_1= 1.4 Hz, J_2= 7.6 Hz, ArH), 7.91 (dd, 1H, J_1= 1.1 Hz, J_2= 8.1 Hz, ArH), 8.27 (d, 1H, *J*= 6.8 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 21.7, 53.3, 107.5, 112.7, 118.1, 118.6, 122.8, 124.6, 124.9, 125.1, 129.0, 129.1, 129.7, 130.3, 132.7, 132.8, 141.4, 142.3, 145.5

mass(ES+) *m/z*= 410.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{19}N_5O_2$: 409.1539. Found: 409.1537.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-methoxyphenyl)prop-2-enenitrile (9f)

Yield: 43% as yellow viscous oil; R_f= 0.21 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (Neat) 2211 (CN), 3384 (NH) cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ= 3.47 (t, 1H, *J*= 5.9 Hz, CH_2NH), 3.76 (d, 2H, *J*= 5.8 Hz, CH_2NH), 3.83 (s, 3H, OCH_3), 6.66 (s, 1H, =CH), 6.84-6.88 (m, 3H, ArH), 7.16-7.22 (m, 1H, ArH), 7.49-7.54 (m, 4H, ArH), 7.57-7.63 (m, 1H, ArH), 7.69 (dd, 1H, J_1= 1.3 Hz, J_2= 7.6 Hz, ArH), 7.89 (dd, 1H, J_1= 1.0 Hz, J_2= 8.0 Hz, ArH), 8.25 (d, 1H, *J*= 6.9 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.3, 55.6, 105.6, 112.7, 114.3, 118.0, 119.0, 122.9, 124.6, 125.0, 125.1, 125.7, 129.0, 131.0, 132.7, 134.5, 142.3, 145.1, 149.5, 161.6

mass (ES+) *m/z*= 426.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{19}N_5O_3$: 425.1488. Found: 425.1492.

(*Z*)-2-({[2-(2-Nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(2,4-dichlorophenyl)prop-2-enenitrile (9g)

Yield: 40% as yellow viscous oil, R_f= 0.25 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (Neat) 2214 (CN), 3381 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.49 (t, 1H, *J*= 3.0 Hz, CH_2NH), 3.83 (d, 2H, *J*= 5.8 Hz, CH_2NH), 6.88-6.93 (m, 1H, ArH), 7.06 (s, 1H, =CH), 7.39 (d, 1H, *J*= 2.1 Hz, ArH), 7.54-7.57 (m, 3H, ArH), 7.60-7.67 (m, 2H, ArH), 7.73-7.74 (m, 2H, ArH), 7.94 (dd, 1H, J_1= 1.1 Hz, J_2= 8.0 Hz, ArH), 8.23-8.26 (m, 1H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.6, 112.9, 113.1, 117.5, 118.1, 122.8, 124.7, 124.8, 125.2, 127.7, 129.2, 129.9, 132.8, 135.1, 137.0, 140.6, 149.6

mass (ES+) *m/z*= 464.2 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{15}Cl_2N_5O_2$: 463.0603. Found: 463.0602.

(*Z*)-2-({[2-(2-Chloro-5-nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-phenylprop-2-enenitrile (10a)

Yield: 50% as a yellow solid, mp 131-132 ^{o}C; R_f= 0.21 (hexanes: EtOAc, 70:30, v/v)

ν_{max} (KBr) 2205 (CN), 3380 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.76 (s, 3H, CH_2NH and CH_2NH), 6.49 (s, 1H, =CH), 6.95 (t, 1H, *J*= 6.5 Hz, ArH), 7.27-7.37 (m, 4H, ArH), 7.42 (d, 2H, *J*= 6.8 Hz, ArH), 7.60 (d, 1H, *J*= 9.1 Hz, ArH), 7.64 (d, 1H, *J*= 8.8 Hz, ArH), 8.09 (dd, 1H, J_1= 2.7 Hz, J_2= 8.8 Hz, ArH), 8.31 (d, 1H, *J*= 6.8 Hz, ArH), 8.34 (d, 1H, *J*= 2.7 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.4, 108.2, 112.9, 118.1, 122.8, 123.9, 125.0, 125.4, 127.5, 128.8, 129.0, 131.0, 131.2, 132.5, 134.8, 135.3, 139.3, 142.6, 145.4, 146.5

mass (ES+) *m/z*= 430.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{23}H_{16}ClN_5O_2$: 429.0993. Found: 429.0967.

(*Z*)-2-({[2-(2-Chloro-5-nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(2-chlorophenyl)prop-2-enenitrile (10b):

Yield: 35% as a yellow solid, mp 162-163 ^{o}C; R_f= 0.31 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2205 (CN), 3385 (NH) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 3.81 (brs, 3H, CH_2NH and CH_2NH), 6.93-6.97 (m, 2H, ArH and =CH), 7.20-7.38 (m, 4H, ArH), 7.59-7.68 (m, 3H, ArH), 8.12-8.15 (m, 1H, ArH), 8.31 (d, 1H, *J*= 6.8 Hz, ArH), 8.47 (d, 1H, *J*= 2.2 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 52.7, 111.6, 112.8, 117.1, 118.0, 122.7, 123.9, 124.8, 125.2, 127.1, 127.5, 128.5, 129.9, 130.7, 130. 9, 131.7, 134.2, 134.5, 135.2, 139.2, 141.5, 142.5, 146.5

mass (ES+) *m/z*= 464.1 $[M+1]^+$

Anal. Calcd. for $C_{23}H_{15}Cl_2N_5O_2$; C, 59.50; H, 3.26; N, 15.08. Found C, 59.69; H, 3.45; N, 14.84.

(*Z*)-2-({[2-(2-chloro-5-nitrophenyl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-(4-methylphenyl)prop-2-enenitrile (10d):

Yield: 40% as a yellow solid, mp 162-163 ^{o}C; R_f= 0.25 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2212 (CN), 3282 (NH) cm^{-1}

^{1}H NMR (200 MHz, $CDCl_3$) δ= 2.35 (s, 3H, CH_3), 3.70-3.80 (m, 3H, CH_2NH and CH_2NH), 6.40 (s, 1H, =CH), 6.95 (dt, 1H, J_1= 0.8 Hz, J_2= 6.8 Hz, ArH), 7.19 (d, 2H, *J*= 8.2 Hz, ArH), 7.24-7.29 (m, 2H, ArH), 7.33 (s, 1H, ArH), 7.62 (t, 2H, *J*= 8.5 Hz, ArH), 8.07 (dd, 1H, J_1= 2.8 Hz, J_2= 8.8 Hz, ArH), 8.29-8.32 (m, 2H, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 21.5, 53.3, 106.6, 112.7, 118.0, 118.1, 122.7, 123.8, 124.9, 125.2, 127.4, 128.7, 129.5, 129.7, 130.8, 134.7, 135.2, 139.0, 141.9, 142.5, 145.3, 146.4

mass (ES+) *m/z*= 444.1 $[M+1]^+$

Anal. Calcd. for $C_{24}H_{18}ClN_5O_2$; C, 64.94; H, 4.09; N, 15.78. Found C, 64.77; H, 4.02; N, 15.91.

(*Z*)-2-({[2-(5-Phenylisoxazol-3-yl)imidazo[1,2-*a*]pyridin-3-yl]amino}methyl)-3-phenylprop-2-enenitrile (11a)

Yield: 36% as a yellow solid, mp 145-146 ^{o}C R_f= 0.30 (hexanes: EtOAc, 70: 30, v/v)

ν_{max} (KBr) 2213 (CN), 3338 (NH) cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ= 4.09 (s, 3H, CH_2NH and CH_2NH), 6.93-6.95 (m, 1H, ArH), 7.11 (s, 1H, ArH), 7.17 (s, 1H, ArH), 7.41-7.58 (m, 8H, ArH), 7.73 (s, 2H, ArH), 7.89 (s, 2H, ArH), 8.41 (d, 1H, *J*= 6.0 Hz, ArH)

^{13}C NMR (75 MHz, $CDCl_3$) δ= 53.9, 99.3, 108.8, 113.1, 117.8, 123.1, 126.0, 126.9, 127.2, 128.9, 128.97, 129.0, 130.2, 130.8, 132.8, 142.6, 145.7

mass (ES+) *m/z*= 418.2 $[M+1]^+$

Anal. Calcd. for $C_{26}H_{19}N_5O$; C, 74.80; H, 4.59; N, 16.78. Found C, 74.99; H, 4.45; N, 16.76.

General procedure for the synthesis of compounds 13a-g as exemplified for 13a

To a solution of **9a** (0.2 g, 0.50 mmol) in a mixture of THF: water (8.0 mL, 1:1, v/v), In powder (0.176 g, 1.52 mmol) was added followed by drop wise addition of 0.24 mL of concentrated HCl and the reaction was allowed to stir at room temperature for 1 h. On completion the THF was removed, EtOAc (10mL) was added to the residue and the solution was neutralized with saturated $NaHCO_3$ solution. The mixture was passed through a celite bed

with EtOAc. The organic layer was separated and the aqueous layer was further extracted with EtOAc (3 x 15 ml). The combined organic layers were washed with brine, dried over anhyd. Na_2SO_4 and concentrated to yield the crude product. The crude product was dissolved in THF (6.0 mL) and then CNBr (0.078 g, 0.74 mmol) and K_2CO_3 (0.136 g, 0.98 mmol) were simultaneously added and the reaction mixture was allowed to stir for 9 h. After completion the solvent was removed under vacuo to prvide the crude product which upon column chromatography on silica-gel with MeOH: EtOAc (1:4, v/v) afforded 0.120 g (62%) of **13a** as a yellow solid.

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-phenyl-acrylonitrile (13a)

Yield: 62% as a yellow solid, mp 220-221 ^oC, R_f= 0.20 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2208 (CN), 3417 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 4.15 (d, 2H, *J*= 3.3 Hz, CH_2), 6.56 (s, 1H, ArH), 7.44-7.53 (m, 6H, ArH and =CH), 7.61-7.73 (m, 4H, ArH and NH_2), 7.99 (s, 1H, ArH), 8.27 (t, 1H, *J*= 8.1 Hz, ArH), 8.67 (s, 1H, ArH), 8.92 (d, 1H, *J*= 7.7 Hz, ArH), 9.20 (s, 1H, ArH)

mass (ES+) *m/z*= 391.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{18}N_6$: 390.1593. Found: 390.1574.

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-(2-chloro-phenyl)-acrylonitrile (13b)

Yield: 61% as a yellow solid, mp 231-232 ^oC; R_f= 0.28 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2202 (CN), 3431 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 4.23 (d, 2H, *J*= 5.6 Hz, CH_2), 6.56 (t, 1H, *J*= 5.5 Hz, ArH), 7.42-7.52 (m, 7H, ArH, =CH and NH_2), 7.62-7.68 (m, 2H, ArH), 8.00 (t, 1H, *J*= 6.8 Hz, ArH), 8.30 (t, 1H, *J*= 8.1 Hz, ArH), 8.66 (d, 1H, *J*= 7.4 Hz, ArH), 9.02 (brs, 1H, ArH), 9.18 (d, 1H, *J*= 6.5 Hz, ArH)

mass (ES+) *m/z*= 425.2 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{17}ClN_6$: 424.1203. Found: 424.1205.

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-(4-chloro-phenyl)-acrylonitrile (13c)

Yield: 70% as a yellow solid, mp 210-211 ^oC, R_f= 0.32 (EtOAc: MeOH, 80:20, v/v)

ν_{max} (KBr) 2208 (CN), 3424 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 4.14 (s, 2H, CH_2), 6.63 (s, 1H, ArH), 7.49-7.56 (m, 5H, ArH and =CH), 7.63-7.66 (m, 4H, ArH and NH_2), 7.99 (s, 1H, ArH), 8.28 (t, 1H, *J*= 8.0 Hz, ArH), 8.68 (d, 1H, *J*= 5.6 Hz, ArH), 8.95 (d, 1H, *J*= 7.4 Hz, ArH), 9.25 (s, 1H, ArH)

mass (ES+) *m/z*= 425.2 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{17}ClN_6$: 424.1203. Found: 424.1198

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-(4-fluoro-phenyl)-acrylonitrile (13d)

Yield: 69% as a yellow solid, mp 227-228 ^oC, R_f= 0.26 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2208 (CN), 3411 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 4.13 (d, 2H, *J*= 5.5 Hz, CH_2), 6.47 (s, 1H, ArH), 7.28-7.44 (m, 4H, ArH and =CH), 7.67-7.71 (m, 5H, ArH and NH_2), 7.98 (s, 1H, ArH), 8.29 (d, 1H, *J*= 7.9 Hz, ArH), 8.65 (d, 1H, *J*= 4.7 Hz, ArH), 8.93 (s, 1H, ArH), 9.19 (m, 1H, ArH)

mass (ES+) *m/z*= 409.2 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{17}FN_6$: 408.1499. Found: 408.1501

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-p-tolyl-acrylonitrile (13e)

73% as a yellow solid, mp 218-219 ^oC, R_f= 0.35 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2207 (CN), 3401 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 2.33 (s, 3H, CH_3), 4.14 (s, 2H, CH_2), 6.46 (s, 1H, ArH), 7.25-7.28 (m, 2H, ArH), 7.40-7.70 (m, 7H, ArH, =CH and NH_2), 7.99 (s, 1H, ArH), 8.27 (t, 1H, *J*= 7.5 Hz, ArH), 8.68 (d, 1H, *J*= 7.8 Hz, ArH) 8.90 (d, 1H, *J*= 9.6 Hz, ArH), 9.18 (s, 1H, ArH)

mass (ES+) *m/z*= 405.2 $[M+1]^+$

HR-EIMS Calcd. for $C_{25}H_{20}N_6$: 404.1750. Found: 404.1732.

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-(4-methoxy-phenyl)-acrylonitrile (13f)

Yield: 72% as a yellow solid, mp 209-210 ^oC; R_f= 0.31 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2208 (CN), 3417 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 3.80 (s, 3H, OCH_3), 4.10 (s, 2H, CH_2), 6.97-7.03 (m, 4H, ArH and =CH), 7.37-7.66 (m, 6H, ArH and NH_2), 7.88-7.97 (m, 2H, ArH), 8.28 (d, 1H, *J*= 6.1 Hz, ArH), 8.66-73 (m, 1H, ArH), 9.21 (s, 1H, ArH)

mass (ES+) *m/z*= 391.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{18}N_6$: 390.1593. Found: 390.1574.

2-(6-Amino-5,7,8,12a-tetraaza-dibenzo[a,h]azulen-7-ylmethyl)-3-(2,4-dichloro-phenyl)-acrylonitrile (13g)

Yield: 66% as a yellow solid, mp 224-225 ^oC; R_f= 0.29 (EtOAc: MeOH, 80: 20, v/v)

ν_{max} (KBr) 2215 (CN), 3422 (NH_2) cm^{-1}

^1H NMR (300 MHz, DMSO-d_6) δ= 4.22 (d, 2H, *J*= 5.8 Hz, CH_2), 6.52 (t, 1H, *J*= 5.6 Hz, ArH), 7.42-7.55 (m, 4H, ArH and =CH), 7.63-7.72 (m, 4H, ArH and NH_2), 7.99 (t, 1H, *J*= 7.0 Hz, ArH), 8.29 (t, 1H, *J*= 8.1 Hz, ArH), 8.63 (d, 1H, *J*= 7.5 Hz, ArH), 8.96 (s, 1H, ArH), 9.15 (d, 1H, *J*= 6.3 Hz, ArH)

mass (ES+) *m/z*= 459.1 $[M+1]^+$

HR-EIMS Calcd. for $C_{24}H_{16}Cl_2N_6$ 458.0813. Found: 458.0819.

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