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Synthesis of arylated and aminated naphthalenes and their synthetic applications for aza-heterocycles

Surjeet Singh [a], Ranjay Shaw [a], Shally [a], Sandeep Chaudhary [b], Abhinav Kumar [c], Ramendra Pratap [a,*]

[a] Department of Chemistry, University of Delhi, North Campus, Delhi, 110007, India
[b] Department of Chemistry, MNIT, Jaipur, Rajasthan, 302017, India
[c] Department of Chemistry, University of Lucknow, Lucknow, Uttar Pradesh, 226007, India

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ABSTRACT

We have developed a new, metal free methodology for the synthesis of 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile by reaction of 2-(1-cyano-2,2-bis(methylthio)vinyl)benzonitrile and nitromethane under basic conditions followed by reduction of nitro group. We explored the synthetic potential of 3,4-diamino-2-(methylthio)-1-naphthonitrile for the construction of different class of highly functionalized fused polycyclic *N*-heterocycles, such as 3*H*-naphtho[1,2-*d*]imidazoles, benzo[*f*]quinoxalines and 3*H*-naphtho[1,2-*d*][1,2,3]triazoles. 2-(1-Cyano-2,2-bis(methylthio)vinyl)benzonitrile also provides arylated naphthalenes and carbazole depending on use of functionalized 4-nitrotoluenes as a carbanion source. The structure of some of the compounds was confirmed by single crystal X-ray technique.

1. Introduction

Ketene dithioacetals are versatile intermediates used for the construction of large number of aromatic and heteroaromatic skeletons. These molecules undergo addition, elimination, addition-elimination, and substitution reactions.[1] Their synthetic utility has been explored to construct various aromatic, heteroaromatic, and nonaromatic ring systems of pharmaceutical and medicinal importance.[2] Recently, ketene dithioacetals are used for the synthesis of functionalized 1-amino-2-aroyl/acetylnaphthalenes,[3] partially reduced coumarins,[4] 2*H*-pyran-2-ones,[4] various heterocyclic compounds,[4] and fluorescent molecules.[5]

It is well known that heterocyclic compounds exhibit broad spectrum of medicinal and pharmaceutical applications.[6] Amongst, various heterocycles, nitrogen containing molecules are most widely present in nature. Nitrogen heterocycles are present as whole or substructures in various medicinally important compounds, such as antiproliferative,[7] antihistamines,[8] antimalarial,[9] antiviral,[10] antithrombopoietic,[11] and anti-inflammatory agents.[12] Heterocyclic compounds are also present in dyes[13] and act as key intermediates for the synthesis of organic semiconductors.[14] Various approaches have been established for the synthesis of heterocyclic compounds. 1,2-Diaminoarenes are very important precursor for construction of various N-heterocycles by reaction with ketones and aldehydes.[15] Recently, quinoxaline has been synthesized by using 1,2-phenylenediamine as a precursor under gallium(III) triflate-catalyzed conditions.[16] In another approach α-hydroxy ketones are converted to quinoxalines via metal-catalyzed aerobic oxidation using 2 mol % of $Pd(OAc)_2$ or $RuCl_2(PPh_3)_3$-TEMPO as catalytic system.[17] Vliet et al. have reported the one pot synthesis of benzimidazoles by microwave irradiation.[18] Various bicyclic 2*H*-benzimidazoles have been also synthesized by reaction of various aromatic and heteroaromatic 2-nitroamines, formic acid using iron powder.[19] Some other *N*-heterocycles such as carbazoles were synthesized by intramolecular cross coupling reaction.[20] Substituted biaryls and triazoles by 1,3-dipolar cycloaddition of alkynes and azides.[21] Apart from 1,2-diaminoarenes, [1,1′-biphenyl]-2-amines are also very interesting skeleton. They are present as whole or substructure in various dyes and pigments.[22] From literature it is clear that 1,2-diaminoarenes and [1,1′-biaryl]-2-amines are very interesting precursor used as key intermediate for generating molecular diversity. These molecules have also been used for the formation of various palladium (II) complexes,[23] cyclic urea,[24] and quinones.[25] All these applications gave us impetus to establish a new protocol for the synthesis of highly functionalized [1,1′-biaryl]-2-amines and *o*-diaminonaphthalenes and use them for synthesis of various *N*-heterocycles.

* Corresponding author. Fax: +91 27666646; e-mail address: ramendrapratap@gmail.com (R. Pratap).

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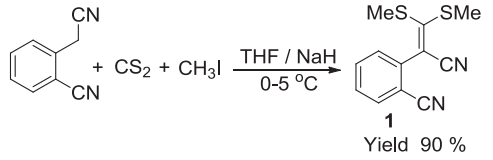
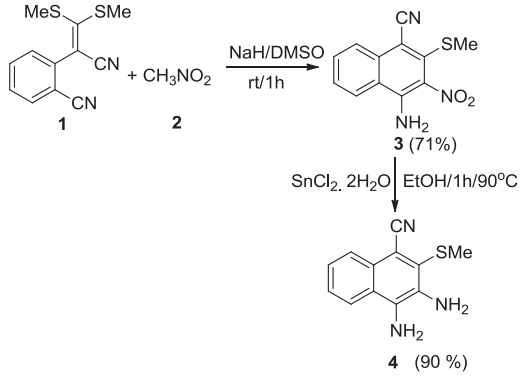
2. Result and discussion

Herein, we wish to report the synthesis of various polyfunctionalized arylated and aminated naphthalenes from 2-(1-cyano-2,2-bis(methylthio)vinyl)benzonitrile (**1**) and their use for construction of different class of aza-heterocycles. Compound **1** is a known compound and was synthesized by reaction of 2-cyanomethyl benzonitrile, carbon disulphide, and methyl iodide under basic conditions in THF (Scheme 1).[3a] Starting from **1** functionalized *o*-diaminonaphthalene **4** was synthesized in a two steps procedure, Scheme 2. In the first step, the reaction of 2-(1-cyano-2,2-bis(methylthio)vinyl)benzonitrile (**1**) and nitromethane (**2**) was performed under basic conditions. An accurate screening of various base solvent combinations revealed that Et_3N/DMSO and NaH/THF combinations were ineffective. Then, we screened sodium hydride, sodium hydroxide, potassium hydroxide, and sodamide as bases in DMF and DMSO as solvents. Under these conditions compound **3** was isolated in 50–71%. Sodium hydride in DMSO gave rise to 4-amino-2-methylsulfanyl-3-nitro-napthalene-1-carbonitrile (**3**) in 71% yield. Then, we performed the reduction[26] of isolated compound **3** using $SnCl_2 \cdot 2H_2O$ in EtOH at 100 °C to afford 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile (**4**) in excellent yield. 3,4-Diaminonaphthalene **4** acts as key intermediate for the synthesis of various heterocyclic compound as reported in Scheme 3.



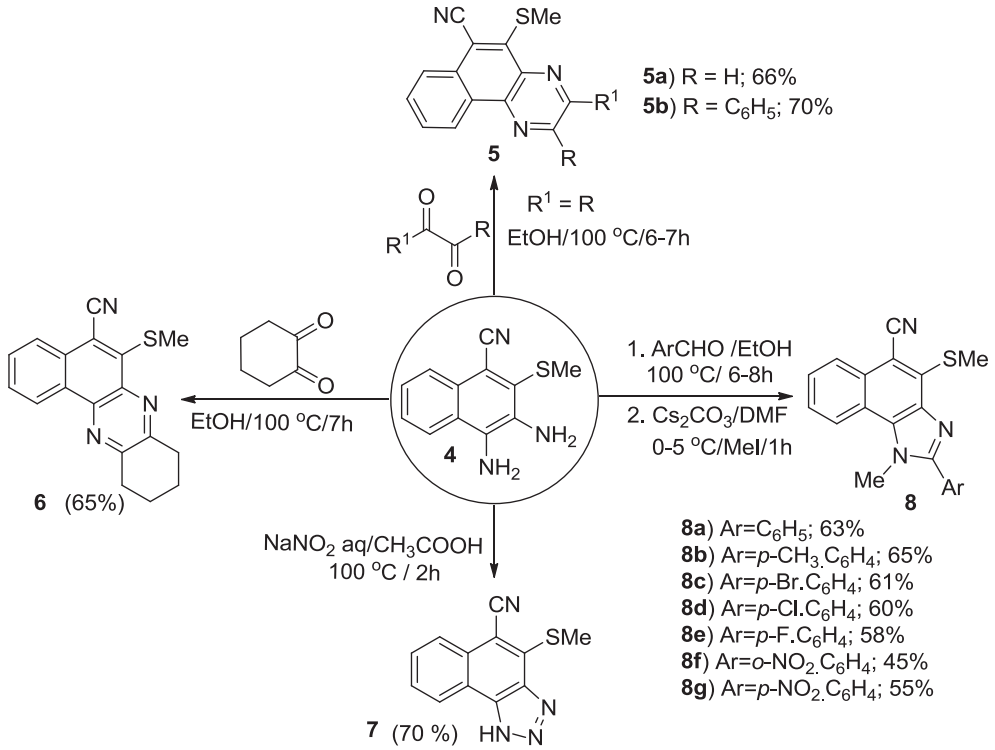
Scheme 1. Synthesis of 2-(1-cyano-2,2-bis(methylsulfanyl-vinyl)benzonitrile **1**.



Scheme 2. Synthesis of 4-amino-2-methylsulfanyl-3-nitro-napthalene-1-carbonitrile **3** and 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile **4**.

We used various diketones as reagents for the synthesis of fused quinoxalines **5a**–**b** and tetrahydrobenzo[*a*]phenazine **6**. We synthesized compounds **5a**–**b** and **6** by reaction of **4** with, respectively, ethane-1,2-dione, diphenylethanone, and cyclohexandione in EtOH at 100 °C. In further exploration, 1-methyl-4-(methylthio)-2-aryl-1*H*-naphtho[1,2-*d*]imidazole-5-carbonitriles (**8a**–**g**) were synthesized in a two steps procedure. Initially, using a literature approach,[27] by reaction of **4** with various functionalized benzaldehydes, 4-(methylthio)-2-aryl-1*H*-naphtho[1,2-*d*]imidazole-5-carbonitriles were prepared. However, due to low solubility, it was difficult to obtain good NMR spectra for these compounds. Thus, to enhance their solubility, these compounds were methylated by using methyl iodide in DMF and cesium carbonate to afford 1-methyl-4-(methylthio)-2-aryl-1*H*-naphtho[1,2-*d*]imidazole-5-carbonitriles (**8a**–**g**). Finally, we have further explored the synthetic utility of **4** for the synthesis of fused triazole **7**. 4-(Methylthio)-1*H*-naphtho[1,2-*d*][1,2,3]triazole-5-carbonitrile **7** was synthesized in 70% yield by reaction of **4** with $NaNO_2$ in acetic acid at 100 °C.

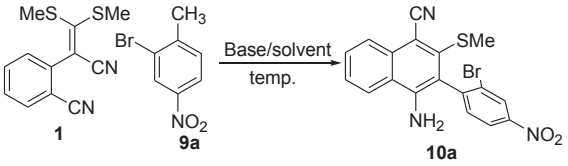
Then, we further explored the synthetic potential of 2-(1-cyano-2,2-bis(methylsulfanyl-vinyl)benzonitrile **1** using functionalized 4-nitrotoluenes **9** as a source of nucleophiles for the synthesis of arylated naphthalenes **10** using a (5+1) annulation



Scheme 3. Synthesis of various fused N-heterocycles (**5**–**8**).

approach, Table 1 and Scheme 4. Initially using **1** and 2-bromo-4-nitrotoluene **9a** as model compounds, we screened various base and solvent combinations for the synthesis of **10a** at various temperatures. We started our screening using sodium hydride as a base

Table 1
Optimization of reaction conditions[a,c]



Entry	Base	Solvent	Time (h)	Yield[b,c] (%)
1	NaH	DMF	5	Complex mixture[b]
2	NaH	DMSO	5	Complex mixture
3	$NaNH_2$	DMSO	5	Complex mixture
4	$NaNH_2$	DMF	5	Complex mixture
5	^{t}BuOK	DMSO	5	Complex mixture
6	^{t}BuOK	DMF	5	Complex mixture[b]
7	KOH	DMF	5	Complex mixture[b]
8	KOH	DMSO	5	Complex mixture
9[d]	KOH	DMSO	2	Complex mixture[b]
10[d]	**KOH**	**DMF**	**2**	**40**
11[d]	NaH	DMSO	2	Trace
12[d]	NaH	DMF	2	35
13[d]	$NaNH_2$	DMF	2	Trace
14[d]	^{t}BuOK	DMF	2	30

[a] Reactions were carried out by stirring 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile (0.5 mmol), 2-Br-1-methyl-4-nitrobenzene (0.55 mmol), base (1.0 mmol) in solvent (4.0 mL) at room temperature.
[b] Incomplete reaction with left starting material.
[c] RT=25–35 °C.
[d] These reactions are carried out at 90 °C. Bold faced line shows optimized reaction condition.

and **9c** the corresponding 4-amino-2-(methylthio)-3-aryl-1-naphthonitriles **10b–c** were obtained in moderate yields. Interestingly, the use of 2-fluoro-1-methyl-4-nitrobenzene **9d** provided 5-(methylthio)-9-nitro-11*H*benzo[*a*]carbazole-6-carbonitrile (**11**) in lieu of the expected 4-amino-3-(2-fluoro-4-nitrophenyl)-2-(methylthio)-1-naphthonitrile. This result is probably related to a concurrent intramolecular cyclization involving NH2 group generated in situ and carbon containing fluoro group. We have also tried 2-methyl-5-nitrobenzonitrile as a nucleophile source, however only a mixture of unidentified compounds was obtained.

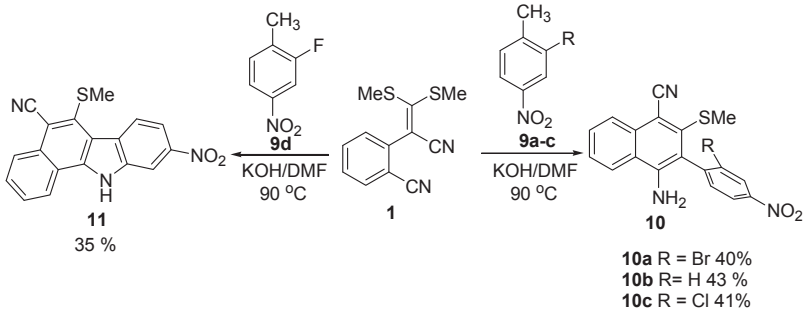
Mechanistically, formation of product 4-amino-2-(methylthio)-3-nitro-1-naphthonitrile (**3**) and 4-amino-2-(methylthio)-3-aryl-1-naphthonitriles **10a–c** involves 5C+1C annulation sequence. From structural investigation of 2-(1-cyano-2,2-bis(methylsulfanyl-vinyl)benzonitrile, it is clear that C2 is more electrophilic due to presence of nitrile and benzonitrile groups at position 1. Initially, the carbanion generated in situ perform Michael addition on C2 of 2-(1-cyano-2,2-bis(methylsulfanylvinyl)benzonitrile followed by loss of methanthiol and formation of intermediates **A** or **A′**. These intermediates in presence of excess of base generate an allylic carbanion able to attack nucleophilically the nitrile group to afford intermediate **B**. Intermediate **B** by tautomerization finally affords the desired product **3** or **10** (see Scheme 5).

We have made several attempt to isolate intermediates **A** or **A′** by shortening the reaction time or using substoichiometric amounts of base. However, all these attempts failed probably because the proposed intermediate, once formed in the reaction mixture, was immediately converted to the reaction product due to presence of active methylene group.

3. X-ray structural analysis

The molecular views (ORTEP) for the both the compounds **5a** and **10a** with atom numbering scheme are presented in Figs. 1 and 2.[28]

In the case of **5a**, the compound crystallizes in the triclinic



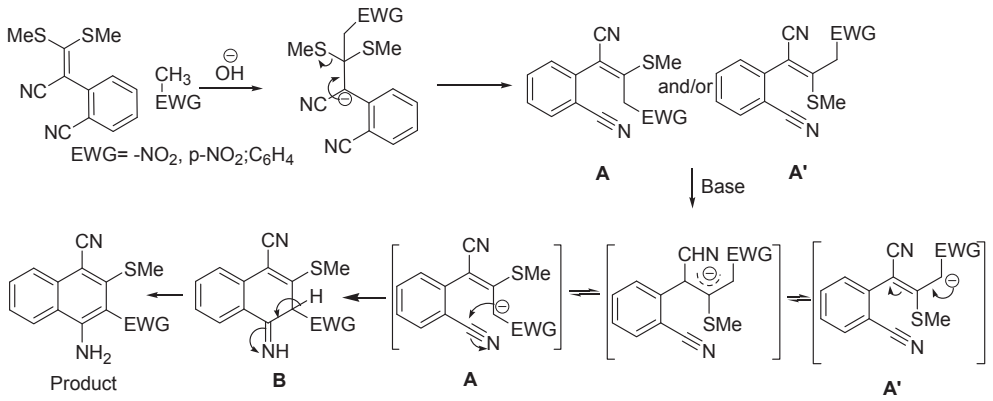
Scheme 4. Synthesis of 4-amino-2-(methylthio)-3-aryl-1-naphthonitrile and 5-(methylthio)-9-nitro-11*H*-benzo[*a*]carbazole-6-carbonitriles.

in DMSO at room temperature. The reaction was carried out for 5 h and formation of a complex mixture observed (Table 1, entry 1). We also tried sodamide, potassium *tert*-butoxide, and potassium hydroxide in DMF and DMSO at room temperature and complex mixture were obtained within variable amount of starting materials (entries 2–9). The screening was then continued at higher temperature (90 °C). Trace amounts of the desired compound **10a** were obtained with NaH in DMSO and with $NaNH_2$ in DMF (entries 11 and 13) while using DMF as reaction medium and KOH, NaH, and ^{t}BuOK as basic compound **10a** was obtained in yields ranging from 30 to 40% (entries 10, 12 and 14).

We then used the optimized reaction conditions reported in Table 1 entry 10 to synthesize some derivatives of arylated naphthalenes, Scheme 4. We used 4-nitrotoluene (**9b**), 2-chloro-4-nitrotoluene (**9c**) 2-fluoro-4-nitrotoluene (**9d**) and as a carbanion source. In case of **9b** system having two molecules in the unit cell. The three fused rings are essentially planar with small dihedral angle of 2.58° between the pyrazine located at one end and phenyl ring at the other terminus.

The dihedral angle between the central ring and the pyrazine ring is 0.94°. The $-SCH_3$ group is deviated by 0.259 Å from the plane of its aromatic ring while the cyano group is in plane with its aromatic ring with slight deviation of 0.066 Å.

In the case of **10a**, there are four molecules in the monoclinic unit cell. The napthalene ring is planar and is almost perpendicular to 2-bromo-4-nitrophenyl ring. The dihedral angle between the naphthyl ring and 2-bromo-4-nitrophenyl ring is 89.32°. In comparison to **5a** the $-SCH_3$ group is in plane of the naphthyl ring and deviated merely by 0.074 Å, while the cyano group is deviated by of 0.171 Å.



Scheme 5. Mechanistic approach for the synthesis of 4-amino-2-methylsulfanyl-3-nitro-napthalene-1-carbonitrile and 4-amino-2-(methylthio)-3-aryl-1-naphthonitriles.

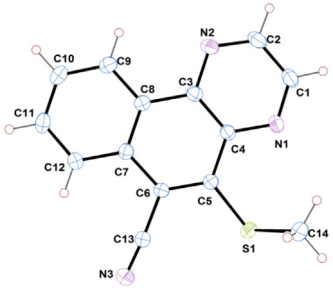


Fig. 1. ORTEP view with atom numbering scheme of compounds **5a** with displacement ellipsoids at the 30% probability level.

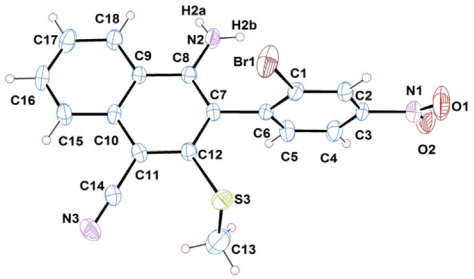


Fig. 2. ORTEP view with atom numbering scheme of compounds **10a** with displacement ellipsoids at the 30% probability level.

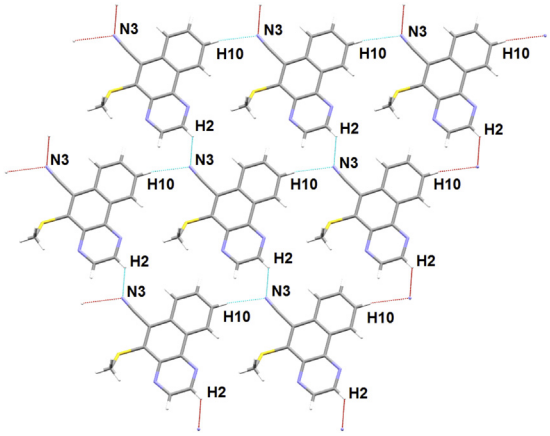


Fig. 3. Supramolecular architecture in **5a** formed by the assistance of weak C–H···N≡C interactions.

The supramolecular aggregations in **5a** are stabilized by a pair of weak (Ar) C–H···N≡C interactions (Fig. 3). The cyano group forms a pair of intermolecular interaction with aromatic hydrogen atoms one from the pyrazine C–H2···N3 (2.731 Å; 126.60°; symm. op. *x*, −1+y, −1+z) and another belonging to the naphthyl ring C–H10···N3 (2.653 Å; 169.85°; symm. op. *x*, −1+y, z). On the basis of the interaction distance and angle parameters it can be said that the second interaction is stronger than that of the first one.

The one dimensional supramolecular aggregations in **10a** are stabilized by weak N–H···N≡C interactions (Fig. 4). The N–H···N≡C interaction distance and angle are 2.38(4) Å and 153.01(4) (symm. op. −1/2+*x*, 3/2−*y*,−1/2+*z*).

4. Conclusions

In summary, we have developed a new simple and efficient route for the synthesis of 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile and 4-amino-2-(methylthio)-3-aryl-1-naphthonitrile by using 2-(1-cyano-2,2-bis(methylsulfanyl-vinyl)benzonitrile as precursor. The synthesized compound 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile act as versatile intermediate and further explored for the synthesis of various heterocyclic compound such as fused quinoxalines, imidazoles and triazoles. Our methodology for the synthesis of 3,4-diamino-2-methylsulfanyl-naphthalene-1-carbonitrile and 4-amino-2-(methylthio)-3-aryl-1-naphthonitrile avoids use of any catalyst, harsh reaction conditions and multistep. 3,4-Diamino-2-methylsulfanyl-naphthalene-1-carbonitrile can be used as precursor for synthesis of large class of heterocycles and some of which is explored here as representative examples. We have also demonstrated the synthesis of 4-amino-2-(methylthio)-3-aryl-1-naphthonitriles, which can be used for synthesis of various biologically potent molecules especially carbazoles. In general, arylation requires suitable precursor, metal catalyzed approach and we have synthesized highly crowded arylated naphthalenes under metal free condition. In conclusion, we can claim that 2-(1-cyano-2,2-bis(methylsulfanyl-vinyl)benzonitrile is very versatile precursor having vast synthetic potential.

5. Experimental

5.1. General

Commercially available reagents from Sigma aldrich and Alfa aesar were used without further purification. ^{1}H and ^{13}C NMR

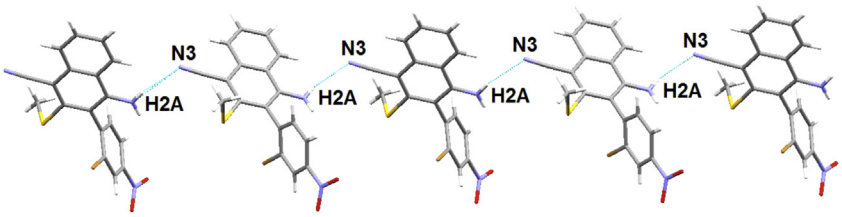


Fig. 4. One dimensional chain motif in **10a** formed by the assistance of weak N–H···N≡C interactions.

spectra were recorded on a 400 MHz NMR and 100 MHz NMR spectrometer and $CDCl_3$ and DMSO-d_6 was used as solvent. Chemical shifts for all the compounds are reported in parts per million shift as δ-value from $CDCl_3$ (δ 7.24 ppm for ^1H and 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are mentioned as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; bs, broad singlet and bm, broad multiplet. Coupling constants (J) for protons are given in hertz (Hz). Infrared (IR) spectra was recorded on a Perkin–Elmer AX-1 spectrophotometer and reported in wave number (cm^{-1}). HRMS reported are showing the peak for MH^+. Synthesis of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile was performed by reported procedure.[3] Intensity data for both the compounds were collected at 298(2) K on an Agilent Xcalibur diffractometer using graphite monochromated Mo-Kα radiation λ=0.71073 Å. Unit cell determination, data collection, and data reduction were performed with CrysAlisPro.[29] The structure was solved by direct methods (SIR97)[30] and refined by a full-matrix least-squares procedure based on F^2.[31] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model. All hetero hydrogen atoms have been located in the difference Fourier map and were refined with bond lengths restraints.

*5.1.1. Synthesis of 4-amino-2-(methylthio)-3-nitro-1-naphthonitrile **3**.* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **1** (0.5 mmol, 0.123 g), nitromethane **2** (0.55 mmol, 0.029 mL) and powdered NaH (1 mmol, 0.024 g) in dry DMSO (4.0 mL) was stirred at room temperature for 1 h under. After completion of reaction, the mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered, washed with cold water and dried over sodium sulfate. The crude product was purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent to afford 71% (0.083 g) of the compound as brown solid. R_f (30% ethylacetate-hexane) 0.29, mp: 217–219 °C; IR (KBr): 3357, 2927, 2216, cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$): δ 2.67 (s, 3H, –S–CH_3), 6.32 (s. 2H, $-NH_2$), 7.65 (t, J=7.7 Hz, 1H, ArH), 7.79 (t, J=7.7 Hz, 1H, ArH), 7.90 (d, J=8.8 Hz, 1H, ArH), 8.19 (d, J=8.8 Hz, 1H, ArH); ^{13}C NMR (100 MH_Z, DMSO): δ 20.0, 100,8, 116.7, 122.1, 124.5, 124.8, 127.5, 131.6, 132.9, 133.1, 135.6, 142.5; HRMS (ESI): (MH^+), found 260.0488, requires $C_{12}H_9N_3O_2S$, 260.0488.

*5.1.2. Synthesis of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4**.* A solution of 4-amino-2-(methylthio)-3-nitro-1-naphthonitrile **3** (0.5 mmol, 0.129 g) in EtOH (5.0 mL) in presence of $SnCl_2{\cdot}2H_2O$ (2.5 mmol, 0.562 g) was refluxed at 90 °C for 1 h. Completion of reaction was monitored by TLC. Excess EtOH was removed under reduced pressure. Crude mixture was poured onto crushed ice and pH was made slightly basic by addition of 10% aqueous sodium bicarbonate. Filter the obtained precipitated and filtrate was extracted with ethyl acetate (30 mL×3). Organic layer was dried over sodium sulfate and crude product was purified by silica gel column chromatography using 35% ethyl acetate in hexane as an eluent to afford 90% (0.103 g) of desired product as brown solid. R_f (40% ethylacetate-hexane) 0.25, mp: 123–124 °C; IR (KBr): 3368, 2932, 2203 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$): δ 2.47 (s, 3H, –S–CH_3), 4.35 (br s, 4H, $-NH_2$) 7.41–7.53 (m, 2H, ArH), 7.64–7.71 (m, 1H, ArH), 8.07–8.13 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 18.9, 105.4, 117.9, 119.9, 122.3, 125.9, 126.0, 126.6, 129.6, 130.1, 130.2, 133.5; HRMS (ESI): (MH^+), found 230.0747, requires for $C_{12}H_{11}N_3S$, 230.0746.

*5.1.3. General procedure synthesis of functionalized benzo[f]quinoxaline-6-carbonitriles **5a**, **5b** and **6**.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 1,2-dicarbonyl compound (0.55 mmol) in EtOH (5.0 mL) was refluxed at 100 °C for 6–7 h. After completion of reaction, desired product was precipitated in ethanol. Cooled the reaction mixture and filtered the obtained precipitate, dried and recrystallized with ethanol.

*5.1.4. 5-(Methylthio)benzo[f]quinoxaline-6-carbonitrile **5a**.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and ethane-1,2-dione (0.55 mmol, 0.025 mL) in EtOH (5.0 mL) was refluxed at 100 °C for 6–7 h. After completion, cooled the reaction mixture and filtered the obtained precipitate, and recrystallized with ethanol to afford the 66% (0.082 g) of light yellow solid. R_f (10% ethylacetate-hexane) 0.42, mp: 175–177 °C; IR (KBr): 2923, 2218 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$): δ 2.86 (s, 3H, –S–CH_3), 7.80–7.91 (m, 2H, ArH), 8.29–8.35 (m, 1H, ArH), 9.00–9.08 (m, 2H, ArH), 9.19–9.24 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 19.6, 115.7, 116.8, 124.9, 125.4, 128.8, 130.2, 130.7, 130.9, 140.7, 142.6, 144.0, 144.5, 145.4; HRMS (ESI): (MH^+); found 252.0590, requires for $C_{14}H_9N_3S$, 252.0590.

*5.1.5. 5-(Methylthio)-2,3-diphenylbenzo[f]quinoxaline-6-carbonitrile **5b**.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and benzil (0.55 mmol, 0.116 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–7 h. After completion, cooled the reaction mixture and filtered the obtained precipitate, dried and recrystallized with ethanol to get 70% (0.143 g) of light yellow solid. R_f (10% ethylacetate-hexane) 0.40, mp: 209–211 °C; IR (KBr): 2928, 2215 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$): δ 2.96 (s, 3H, –S–CH_3), 7.30–7.46 (m, 6H, ArH) 7.60–7.72 (m, 4H, ArH), 7.76–7.88 (m, 2H, ArH), 8.30 (d, J=8.0 Hz, 1H, ArH), 9.26 (d, J=8.0 Hz, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 19.7, 115.2, 116.1, 125.1, 125.4, 128.3, 128.4, 128.5, 129.3, 129.5, 130.0, 130.1, 130.4, 131.1, 138.2, 138.3, 138.4, 139.9, 141.1, 152.5, 153.3; HRMS (ESI): (MH^+); found 404.1216, requires for $C_{26}H_{17}N_3S$, 404.1216.

*5.1.6. 6-(Methylthio)-8,9,10,11-tetrahydrobenzo[a]phenazine-5-carbonitrile **6**.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and cyclohexane-1,2-dione (0.55 mmol, 0.062 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–7 h. After completion, cooled the reaction mixture and filtered the obtained precipitate, dried and recrystallized with ethanol to afford 65% (0.099 g) of yellow solid; R_f (20% ethylacetate-hexane) 0.72, mp: 203–205 °C; IR (KBr): 2951, 2855, 2219 cm^{-1}; ^1H NMR (400 MH_Z, $CDCl_3$): δ 2.02–2.10 (m, 4H, $-CH_2-$), 2.86 (s, 3H,

–S–CH_3), 3.19–3.26 (m, 4H, –CH_2–), 7.71–7.82 (m, 2H, ArH), 8.23–8.27 (m, 1H, ArH), 9.11–9.16 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 19.8, 22.6, 22.6, 32.9, 33.1, 114.6, 116.1, 124.6, 125.2, 128.2, 129.8, 130.1, 130.6, 138.5, 140.0, 143.7, 154.2, 155.3; HRMS (ESI): (MH^+); found 306.1058, requires for $C_{18}H_{15}N_3S$, 306.1059.

5.1.7. Synthesis of 4-(methylthio)-1H-naphtho[1,2-d][1,2,3]triazole-5-carbonitrile ***7***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 gm) and $NaNO_2$ (0.55 mmol) in CH_3COOH (5.0 mL) was heated at 100 °C for 2 h. After completion, excess of CH_3COOH was removed under vacuum. Crude material was neutralized with 10% aqueous solution of sodium bicarbonate. Precipitate obtained was filtered, dried and purified by silica gel column chromatography using 30% ethylacetate in hexane as an eluent to afford 70% (0.084 g) of brown solid. R_f (30% ethylacetate-hexane) 0.22, mp: 212–214 °C; IR (KBr): 3448, 2925, 2221 cm^{-1}; ^{1}H NMR (400 MH_Z, DMSO-d_6): δ 3.08 (s, 3H, –S–CH_3), 3.15 (s, 1H, –NH–), 7.78–7.90 (m, 2H, ArH), 8.10–8.14 (m, 1H, ArH), 8.46 (d, *J*=7.3 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 17.6, 116.0, 123.3, 124.9, 128.2, 129.5, 130.1; HRMS (ESI): (MH^+) found 241.0540, requires for $C_{12}H_8N_4S$, 241.0542.

*5.1.8. General procedure for the synthesis of 1-methyl-4-(methylthio)-2-aryl-1H-naptho[1,2-d]imidazole-5-carbonitrile (****8a–g****).* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and substituted benzaldehyde (0.55 mmol) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. After completion, obtained precipitate was filtered and dried under vacuum. Due to lack of solubility of 4-(methylthio)-2-aryl-1*H*-naphtho[1,2-*d*]imidazole-5-carbonitrile characterization was very difficult. In further step crude product obtained was directly methylated. We have stirred a mixture of 4-(methylthio)-2-aryl-1*H*-naphtho[1,2-*d*]imidazole-5-carbonitrile (0.5 mmol) and MeI (0.55 mmol) and Cs_2CO_3 in THF at 0–5 °C for 1 h. After completion of reaction, excess of THF was removed under vacuum. The mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered, dried and purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent.

5.1.9. 1-Methyl-4-(methylthio)-2-phenyl-1H-naptho[1,2-d]imidazole-5-carbonitrile ***8a***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and benzaldehyde (0.55 mmol, 0.056 mL) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum and crude was methylated by stirring with MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF at 0–5 °C for 1 h. After completion of reaction, excess of THF was removed under vacuum. The mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered, dried and purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent and isolated 63% (0.103 g) golden color solid. R_f (25% ethylacetate-hexane) 0.32, mp: 182–184 °C; IR (KBr): 2919, 2204 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.96 (s, 3H, –S–CH_3), 4.27 (s, 3H, –N–CH_3), 7.52–7.65 (m, 5H, ArH), 7.73–7.79 (m, 2H, ArH), 8.28–8.33 (m, 1H, ArH), 8.39–8.44 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 18.6, 36.1, 106.6, 117.4, 120.5, 121.4, 126.5, 126.5, 126.8, 128.8, 129.2, 129.9, 130.1, 130.6, 132.4, 137.7, 139.7, 154.6; HRMS (ESI): (MH^+); found 330.1065, requires for $C_{20}H_{15}N_3S$, 330.1059.

5.1.10. 1-Methyl-4-(methylthio)-2-(p-tolyl)-1H-naphtho[1,2-d]imidazole-5-carbonitrile ***8b***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 4-methylbenzaldehyde (0.55 mmol, 0.065 mL) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Cooled the reaction mixture and filtered the obtained product and proceed for methylation by stirring the crude, MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF at 0–5 °C for 1 h. After completion of reaction, excess of THF was removed under vacuum. The mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered, dried and purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent to obtain 65% (0.111 g) of orange solid. R_f (25% ethylacetate-hexane) 0.30, mp: 214–216 °C; IR (KBr): 2919, 2203 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.45 (s, 3H, –CH_3), 2.97 (s, 3H, –S–CH_3), 4.26 (s, 3H, –N–CH_3), 7.35 (d, *J*=7.9 Hz, 2H, ArH) 7.53–7.70 (m, 4H, ArH), 8.32–8.37 (m, 1H, ArH), 8.39–8.45 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 18.6, 21.4, 36.2, 106.5, 117.4, 120.5, 121.5, 126.3, 126.4, 126.6, 126.7, 129.4, 129.8, 130.6, 132.4, 137.6, 139.8, 140.4, 154.8; HRMS (ESI): (MH^+); found 344.1220, requires for $C_{21}H_{17}N_3S$, 344.1216.

5.1.11. 2-(4-Bromo-phenyl)-1-methyl-4-methylsulfanyl-1H-naptho[1,2-d]imidazole-5-carbonitrile ***8c***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 4-bromobenzaldehyde (0.55 mmol, 0.102 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum. Further, a mixture of crude, MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF was stirred at 0–5 °C for 1 h. After completion of reaction, excess of THF was removed under vacuum. The mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered, dried and purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent and isolated 61% (0.124 g) of orange solid. R_f (30% ethylacetate-hexane) 0.38, mp: 267–269 °C; IR (KBr): 2922, 2203 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.96 (s, 3H, –S–CH_3), 4.28 (s, 3H, –N–CH_3), 7.63–7.73 (m, 6H, Ar–H), 8.36–8.46 (m, 2H, Ar–H); HRMS (ESI): (MH^+); found 408.0162, requires for $C_{20}H_{14}BrN_3S$, 408.0165.

5.1.12. 2-(4-Chlorophenyl)-1-methyl-4-(methylthio)-1H-naphtho[1,2-d]imidazole-5-carbonitrile ***8d***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 4-chlorobenzaldehyde (0.55 mmol, 0.078 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum. Further, a mixture crude, MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF was stirred at 0–5 °C for 1 h. Usual work-up purification by silica gel column chromatography using 20% ethylacetate in hexane as an eluent provides 60% (0.108 g) of yellow solid; R_f (30% ethylacetate-hexane) 0.42, mp: 185–187 °C; IR (KBr): 2918, 2211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H, –S–CH_3), 4.30 (s, 3H, –N–CH_3), 7.52–7.57 (m, 2H, ArH) 7.61–7.75 (m, 4H, ArH), 8.25–8.29 (dd, *J*=1.4 Hz, 1H, ArH), 8.64–8.71 (m, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 21.3, 35.2, 113.1, 117.2, 122.6, 125.5, 126.3, 127.3, 127.6, 127.9, 128.1, 129.2, 130.2, 131.2, 131.4, 136.6, 142.2, 155.3; HRMS (ESI): (MH^+); found 364.0676, requires for $C_{20}H_{14}ClN_3S$, 364.0670.

5.1.13. 2-(4-Fluorophenyl)-1-methyl-4-(methylthio)-1H-naphtho[1,2-d]imidazole-5-carbonitrile ***8e***. A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 4-fluorobenzaldehyde (0.55 mmol, 0.059 mL) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum. In further step we have stirred the crude mixture, MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF at 0–5 °C for 1 h. Usual work-up and purification over silica gel column chromatography using 20% ethylacetate in hexane as an eluent provides 58% (0.100 g) of yellow solid. R_f (30% ethylacetate-hexane) 0.40, mp: 184–186 °C; IR (KBr): 2921, 2207 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3H, –S–CH_3), 4.31 (s, 3H,

–N–CH_3), 7.21–7.31 (m, 2H, ArH) 7.62–7.72 (m, 2H, ArH), 7.74–7.83 (m, 2H, ArH), 8.26–8.32 (m, 1H, ArH), 8.67–8.72 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 35.2, 112.2, 116.1(d, J_{C-F}=22.0 Hz), 117.3, 122.6, 125.6, 125.6, 126.3, 127.3, 127.6, 128.1, 130.2, 131.4, 132.0 (d, J_{C-F}=8.6 Hz), 142.3, 155.5, 163.8 (d, J_{C-F}=248.2 Hz); HRMS (ESI): (MH^+); found 348.0976, requires for $C_{20}H_{14}FN_3S$, 348.0965.

5.1.14. 1-Methyl-4-(methylthio)-2-(2-nitrophenyl)-1H-naptho[1,2-d] imidazole-5-carbonitrile ***8f****.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 2-nitrobenzaldehyde (0.55 mmol, 0.084 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum. In further step, stirred the crude mixture, (0.5 mmol, 0.181 g), MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF at 0–5 °C for 1 h. Usual work-up and purification by silica gel column chromatography using 20% ethylacetate in hexane as an eluent afforded 45% (0.084 g) of brown solid. R_f (30% ethylacetate-hexane) 0.30, mp: 309–311 °C; IR (KBr): 2919, 2203 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.86 (s, 3H, –S–CH_3), 4.09 (s, 3H, –N–CH_3), 7.62–7.88 (m, 5H, ArH), 8.24–8.29 (dd, J=1.5 Hz, 1H, ArH), 8.35–8.45 (m, 2H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 18.7, 35.1, 107.5, 117.2, 120.6, 121.5, 125.0, 125.3, 126.8, 126.9, 127.1, 130.9, 131.5, 131.7, 133.2, 133.7, 137.8, 139.8, 148.9, 150.1; HRMS (ESI): (MH^+); found 375.0915, requires for $C_{20}H_{14}N_4O_2S$, 375.0910.

5.1.15. 1-Methyl-4-methylsulfanyl-2-(4-nitro-phenyl)-1H-naptho [1,2-d]imidazole-5-carbonitrile ***8g****.* A mixture of 3,4-diamino-2-(methylthio)-1-naphthonitrile **4** (0.5 mmol, 0.114 g) and 4-nitrobenzaldehyde (0.55 mmol, 0.084 g) in EtOH (5.0 mL) was refluxed at 100 °C for 6–8 h. Obtained precipitate was filtered and dried under vacuum. In further step, stirred the crude, MeI (0.55 mmol, 0.035 mL) and Cs_2CO_3 in THF at 0–5 °C for 1 h. Usual work-up and purification by silica gel column chromatography using 20% ethylacetate in hexane as an eluent afforded 55% (0.102 g) of brown solid. R_f (30% ethylacetate-hexane) 0.32, mp: 267–269 °C; IR (KBr): 2925, 2210 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.69 (s, 3H, –S–CH_3), 4.39 (s, 3H, –N–CH_3), 7.67–7.77 (m, 2H, ArH), 8.02 (d, J=8.8 Hz, 2H, ArH), 8.32 (d, J=8.7 Hz, 1H, ArH), 8.44 (d, J=8.0 Hz, 2H, ArH), 8.69–8.75 (m, 1H, ArH); HRMS (ESI): (MH^+); found 375.0916, requires for $C_{20}H_{14}N_4O_2S$, 375.0910.

*5.1.16. General procedure synthesis of 4-amino-2-(methylthio)-3-aryl-1-naphthonitrile (****10a–c****).* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **1** (0.5 mmol, 0.123 g) and 2-Br/Cl/H-1-methyl-4-nitrobenzene (0.55 mmol) and powdered KOH (1 mmol, 0.056 g) in dry DMF (4.0 mL) was stirred at 90 °C for 2 h. Reaction was monitored by TLC. After completion, reaction mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered and dried. The crude product was purified by silica gel column chromatography using 20% ethyl acetate in hexane as an eluent.

5.1.17. 4-Amino-3-(2-bromo-4-nitrophenyl)-2-(methylthio)-1-naphthonitrile ***10a****.* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **1** (0.5 mmol, 0.123 g), 2-bromo-1-methyl-4-nitrobenzene (0.55 mmol, 0.119 g) and powdered KOH (1 mmol, 0.056 g) in dry DMF (4.0 mL) was stirred at 90 °C for 2 h. Usual work-up and purification by silica gel column chromatography using 20% ethyl acetate in hexane as an eluent provides 40% (0.082 g) of brown solid. R_f (20% ethylacetate-hexane) 0.31, mp: 136–138 °C; IR (KBr): 2917, 2209 cm^{-1}; ^{1}H NMR (400 MH_Z, $CDCl_3$): δ 2.46 (s, 3H, –S–CH_3), 4.47 (s, 2H, –NH_2), 7.48 (d, J=8.0 Hz, 1H, ArH), 7.57–7.63 (m, 1H, ArH), 7.72 (t, J=8.0 Hz, 1H, ArH), 7.81 (d, J=8.8 Hz, 1H, ArH), 8.25 (d, J=8.8 Hz, 1H, ArH), 8.32–8.42 (dd, J=2.2 Hz, 1H, ArH), 8.63 (d, J=2.2 Hz, 1H, ArH); ^{13}C NMR (100 MH_Z, $CDCl_3$): δ 19.9, 104.6, 117.4, 121.4, 121.5, 123.1, 126.0, 126.4, 126.9, 128.5, 129.6, 133.2, 134.4, 141.6, 143.3, 144.6, 148.2; HRMS (ESI): (MH^+); found 413.9907, requires for $C_{18}H_{12}BrN_3O_2S$, 413.9906.

5.1.18. 4-Amino-2-(methylthio)-3-(4-nitrophenyl)-1-naphthonitrile ***10b****.* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **1** (0.5 mmol, 0.123 g), 4-nitrotoluene (0.55 mmol, 0.076 g) and powdered KOH (1 mmol, 0.056 g) in dry DMF (4.0 mL) was stirred at 90 °C for 2 h. Usual work-up and purification by silica gel column chromatography using 20% ethyl acetate in hexane as an eluent afforded 43% (0.072 g) of brown solid. R_f (20% ethylacetate-hexane) 0.32. Mp: 282–284 °C; IR (KBr): 2922, 2213 cm^{-1}; ^{1}H NMR (400 MH_Z, DMSO): δ 2.24 (s, 3H, –S–CH_3), 6.38 (s, 2H, –NH_2), 7.53–7.63 (m, 3H, ArH) 7.71–7.78 (m, 1H, ArH), 7.98 (d, J=8.8 Hz, 1H, ArH), 8.32–8.42 (m, 3H, ArH); ^{13}C NMR (100 MH_Z, DMSO): δ 19.3, 99.8, 117.8, 120.6, 121.1, 123.7, 124.1, 124.3, 125.9, 129.5, 132.5, 133.7, 140.8, 144.4, 146.6, 147.0; HRMS (ESI): (MH^+); found 336.0800, requires for $C_{18}H_{13}N_3O_2S$, 336.801.

5.1.19. 4-Amino-3-(2-chloro-4-nitrophenyl)-2-(methylthio)-1-naphthonitrile ***10c****.* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **1** (0.5 mmol, 0.123 g), 2-chloro-1-methyl-4-nitrobenzene (0.55 mmol, 0.095 g) and powdered KOH (1 mmol, 0.056 g) in dry DMF (4.0 mL) was stirred at 90 °C for 2 h. Usual work-up and purification by silica gel column chromatography using 20% ethyl acetate in hexane as an eluent provides 41% (0.075 g) of brown solid. R_f (20% ethylacetate-hexane) 0.29, mp: 134–136 °C; IR (KBr): 2916, 2207 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO): δ 2.39 (s, 3H, –S–CH_3), 4.43 (s, 2H, –NH_2), 7.45 (d, J=8.0 Hz, 1H, ArH), 7.52–7.58 (m, 1H, ArH), 7.64–7.71 (m, 1H, ArH), 7.76 (d, J=8.0 Hz, 1H, ArH), 8.18–8.26 (m, 2H, ArH), 8.42 (d, J=2.2 Hz, 1H, ArH); ^{13}C NMR (100 MHZ, DMSO): δ 19.9, 104.8, 117.3, 119.6, 121.4, 121.4, 122.5, 125.4, 126.1, 127.0, 129.6, 133.4, 134.4, 136.4, 141.6, 142.3, 143.5, 148.3; HRMS (ESI): (MH^+); found 370.0418, requires for $C_{18}H_{12}ClN_3O_2S$, 370.0412.

5.1.20. Synthesis of 6-(methylthio)-9-nitro-11H-benzo[a]carbazole-5-carbonitrile ***11****.* A mixture of 2-(1-cyno-2,2-bismethylsulfanyl-vinyl)-benzonitrile **2** (0.5 mmol, 0.123 g), 2-fluoro-1-methyl-4-nitrobenzene (0.5 mmol, 0.085 g) and powdered KOH (1 mmol, 0.056 g) in dry DMF (4.0 mL) was stirred at 90 °C for 2 h. After completion of reaction, the mixture was poured onto ice-water with constant stirring followed by neutralization with 10% HCl. The obtained precipitate was filtered and dried. The crude product was purified by silica gel column chromatography using 20% ethylacetate in hexane as an eluent and 35% (0.058 g) of white solid was isolated; R_f (20% ethylacetate-hexane) 0.21, mp: 339–341 °C; IR (KBr): 3335, 2925, 2205 cm^{-1}; ^{1}H NMR (400 MH_Z, DMSO): δ 2.68 (s, 3H, –S–CH_3), 7.86–7.93 (m, 2H, ArH), 8.17–8.24 (m, 2H, ArH), 8.46 (d, J=2.2 Hz, 1H, ArH), 8.60–8.66 (m, 1H, ArH), 8.83 (d, J=8.8 Hz, 1H, ArH), 13.4 (s, 1H, -NH-); ^{13}C NMR (100 MHz, DMSO): δ 19.9, 107.1, 107.7, 115.4, 116.4, 117.0, 120.0, 122.6, 123.1, 125.2, 127.1, 127.9, 129.4, 131.2, 138.1, 138.3, 140.8, 144.4; HRMS (ESI): (MH^+); found 334.0649, requires for $C_{18}H_{11}N_3O_2S$, 334.0645.

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Supplementary data

Supplementary data related to this article can be found, in the online version at http://dx.doi.org/10.1016/j.tet.2016.08.044.

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28. Crystal Data **5a** (CCDC 1422163): $C_{14}H_9N_3S$, M=251.30, Triclinic, P−1, a=7.3493(13) Å, b=9.3049(19) Å, c=10.0874(19) Å, α=115.323(19)° β=108.578(16)°, γ=91.193(16)°, V=581.0(2) Å^3, Z=2, D_{calcd}=1.436 mg m^{-3}, F(000)=260, crystal size 0.400×0.180×0.150 mm, reflections collected 4300, independent reflections 2442 [$R_{(int)}$=0.0148], Final indices [$I>2\sigma(I)$] R_1=0.0368 wR_2=0.1009, R indices (all data) R_1=0.0416, wR_2=0.1055, gof 1.059, Largest difference peak and hole 0.211 and −0.207 e Å^{-3}.Crystal Data **10a** (CCDC 1422164): $C_{18}H_{12}BrN_3O_2S$, M=414.28, Monoclinic, P 21/n, a=10.8942(17) Å, b=11.515(3) Å, c=14.123(2) Å, β=90.653(15)°, V=1771.5(6) Å^3, Z=4, D_{calcd}=1.553 mg m^{-3}, F(000)=832, crystal size 0.230×0.200×0.180 mm, reflections collected 7469, independent reflections 3523 [$R_{(int)}$=0.0273], Final indices [$I>2\sigma(I)$] R_1=0.0644 wR_2=0.1233, R indices (all data) R_1=0.1068, wR_2=0.1412, gof 1.030, Largest difference peak and hole 0.616 and −0.402 e Å^{-3}.
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