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An improved and clean procedure for the synthesis of one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety in aqueous media catalyzed by TEBAC in the presence and absence of K_2CO_3

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Abstract—A clean and simple synthesis of one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety was accomplished via the reaction of 1-arylethylidenemalonodinitriles with arylidenemalonodinitriles in aqueous media catalyzed by TEBAC in the presence of K_2CO_3. The important intermediates were obtained successfully to confirm the mechanism in the absence of base under the same reaction conditions. The structures of **3m** and **4b** were confirmed by X-ray diffraction studies.

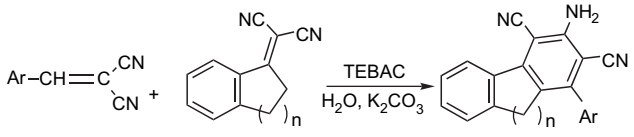
1. Introduction

In the past decades, much research effort has been devoted to the investigation of the acceptor–donor–acceptor (A–D–A) systems,[1] for their comprising one electron donor and two electron acceptors in the extensive study of photo-induced intra-molecular electron transfer, which inspired by the molecule in which electron transfer can be approached comprises a single donor and a single acceptor. This considerable research effort is justified by the potential applications of these molecular systems, which are the basis for artificial photosynthetic systems,[2] materials presenting semiconducting or nonlinear optical properties[3] and molecular electronic devices.[4] 2,6-Dicyanoanilines are typical A–D–A systems and they have been reported to be prepared from arylidenemalonodinitriles and 1-arylethylidenemalonodinitriles in the presence of piperidine[5] or under microwave irradiation.[6] The reaction between propanedinitrile and α,β-unsaturated ketones could also give 2,6-dicyanoanilines, but the yields were very poor.[7] All the above-mentioned reactions were performed in organic solvents.

As part of our current studies on the development of organic reactions in aqueous media,[8] which have been considered as very promising and attractive substitutes for volatile organic solvents and widely used in the Green Chemistry area. Since Breslow,[9] who showed that hydrophobic effects could strongly enhance the rate of several organic reactions, rediscovered the use of water as a solvent in organic chemistry in 1980s. We now report an efficient and clean synthetic route to the one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety in water catalyzed by TEBAC (triethylbenzylammonium chloride) in the presence and absence of K_2CO_3 at 50 °C.

2. Results and discussion

When the reaction of arylidenemalonodinitriles **1** and 2-(2,3-dihydronaphthalen-4(1*H*)ylidene)malononitrile or 2-(2,3-dihydroinden-3-ylidene)malononitrile **2** was carried out in water at 50 °C in the presence of K_2CO_3 (Scheme 1), the highly substituted fluorene and phenanthrene derivatives containing 2,6-dicyanoaniline moiety with one donor and two acceptors were obtained as expected in high yields.



1 2 3

Scheme 1.

In our initial study, the reaction of 4-chlorophenylidenemalonodinitrile **1a** and 2-(2,3-dihydronaphthalen-4(1*H*)-ylidene) malononitrile **2** was used as a model reaction to

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Table 1. Synthesis of **3a** in water under different reaction conditions[a]

Entry	*T*/°C	Amount/mol %	Catalyst	Yield[b]/%
1	rt	0	—	0
2	50	0	—	Trace
3	rt	20	TEBAC	Trace
4	40	20	TEBAC	63
5	50	20	TEBAC	86
6	60	20	TEBAC	83
7	50	10	TEBAC	80
8	50	30	TEBAC	85
9	50	20	$CH_3(CH_2)_{15}NMe_3Br$	82
10	50	20	$CH_3(CH_2)_{11}SO_3Na$	84

[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), TEBAC (20 mol %), K_2CO_3 (4 mmol), water (10 mL).
[b] Isolated yields.

optimize the conditions. The reaction was first carried out in water in the absence of TEBAC. No reaction occurred at room temperature (Table 1, entry 1), while only trace amount of product **3a** was observed by TLC when the reaction temperature was raised to 50 °C (Table 1, entry 2). Similar reactions were then attempted in the presence of 10, 20 and 30 mol % of TEBAC. The results from Table 1 (entries 5, 7 and 8) showed that 20% TEBAC at 50 °C in water was sufficient to push the reaction forward. Higher loading of the catalyst did not improve the reaction condition to a great extent. To find the optimum reaction temperature, the reaction was carried out with 20 mol % of TEBAC at room temperature, 40, 50 and 60 °C, resulting in the isolation of **3a** in trace amount, 63%, 86% and 83% yields (Table 1, entries 3–6), respectively. Thus, 20 mol % of TEBAC and a reaction temperature at 50 °C were optimal conditions. In addition, $CH_3(CH_2)_{15}NMe_3Br$ and $CH_3(CH_2)_{11}SO_3Na$ (Table 1, entries 9 and 10) were also tested as the catalysts. In these cases, product **3a** was formed in slightly lower yield (Table 1, entries 9 and 10). We also tested the three components reaction of 4-chlorobenzaldehyde, malononitrile and 1-tetralone, but the desired product was not detected. Perhaps 2-(2,3-dihydronaphthalen-4(1*H*)ylidene) malononitrile **2** was not formed in the aqueous media. The catalyst TEBAC could be reused for the synthesis of **3a** without significant loss of activity. The results are summarized in Table 2.

In order to apply this reaction to a library synthesis, various kinds of arylidenemalonodinitriles **1** and **2** were subjected to give the corresponding fluorene and phenanthrene derivatives containing 2,6-dicyanoaniline moiety **3**, and representative examples are shown in Table 3. All of **1** gave expected products in good to high yields, either bearing electron-withdrawing groups (such as halide, nitro) or electron-donating groups (such as alkyl group, alkoxyl group) under same reaction conditions.

Although the detailed mechanism of the above reaction has not been clarified yet, the formation of fluorene and

Table 2. Reuse of the catalyst for synthesis of **3a**[a]

Round	1	2	3	4
Yield[b]	86	87	87	85

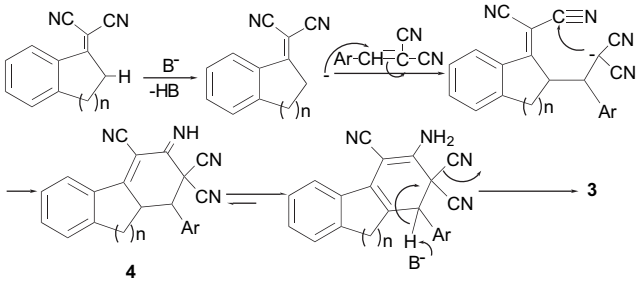
[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), K_2CO_3 (2 mmol), water (10 mL).
[b] Isolated yields.

Table 3. TEBAC catalyzed reaction of **1** and **2** in the presence of K_2CO_3[a]

Entry	Ar	*n*	Time/h	Yields[b]/%
3a	$4\text{-}ClC_6H_4$	2	12	86
3b	$4\text{-}FC_6H_4$	2	10	89
3c	$2\text{-}ClC_6H_4$	2	10	92
3d	$3\text{-}ClC_6H_4$	2	10	90
3e	$4\text{-}CH_3C_6H_4$	2	14	85
3f	$4\text{-}BrC_6H_4$	2	14	86
3g	$2,4\text{-}Cl_2C_6H_3$	2	10	86
3h	$3,4\text{-}(CH_3O)_2C_6H_4$	2	14	84
3i	$2,4\text{-}Cl_2C_6H_3$	1	8	90
3j	$4\text{-}BrC_6H_4$	1	9	90
3k	$4\text{-}FC_6H_4$	1	8	84
3l	$4\text{-}ClC_6H_4$	1	8	86
3m	$3,4\text{-}(CH_3O)_2C_6H_4$	1	10	84
3n	$4\text{-}NO_2C_6H_4$	1	8	90
3o	$3,4\text{-}Cl_2C_6H_3$	1	8	89

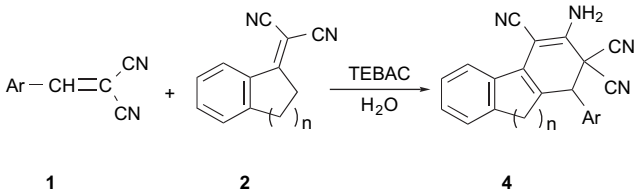
[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), TEBAC (20 mol %), K_2CO_3 (4 mmol), water (10 mL), 50 °C.
[b] Isolated yields.

phenanthrene derivatives **3** can be tentatively explained by the pathway presented in Scheme 2.



Scheme 2.

As shown in Scheme 2, we believe that the deprotonation with K_2CO_3 followed by the elimination of CN may take place in the last step to afford final product **3**. In order to obtain immediates **4**, we ran the same reactions in the absence of K_2CO_3 to support our proposed mechanism (Scheme 3). To our delight, the reactions proceeded smoothly and the desired products **4** containing one donor and three acceptors were isolated in high yields. The results are summarized in Table 4.



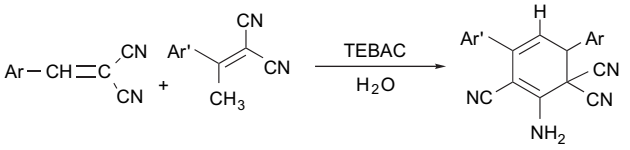
Scheme 3.

Encouraged by this result, the 1-arylethylidenemalonodinitriles **5** were reacted with arylidenemalonodinitriles **1** in aqueous media catalyzed by TEBAC in the absence of K_2CO_3 to give 2-amino-4,6-diarylcyclohexa-2,4-diene-1,1,3-tricarbonitrile derivatives **6** containing one donor and three acceptors as expected in high yields (Scheme 4). The results are summarized in Table 5.

Table 4. TEBAC catalyzed reaction of **1** and **2** in the absence of K_2CO_3[a]

Entry	Ar	*n*	Time/h	Yields[b]/%
4a	4-ClC_6H_4	2	8	92
4b	3-ClC_6H_4	2	7	84
4c	4-$CH_3OC_6H_4$	2	10	88
4d	4-BrC_6H_4	2	8	90
4e	3-$NO_2C_6H_4$	2	6	94
4f	2,4-$Cl_2C_6H_3$	2	6	90
4g	3,4-$(CH_3)_2C_6H_3$	2	10	83
4h	4-FC_6H_4	1	7	89
4i	3,4-$Cl_2C_6H_3$	1	8	92
4j	2,4-$Cl_2C_6H_3$	1	6	85
4k	4-ClC_6H_4	1	8	92
4l	2-$CH_3OC_6H_4$	1	10	82
4m	2-$NO_2C_6H_4$	1	6	93
4n	4-$CH_3C_6H_4$	1	10	86

[a] Reagents and conditions: **1** (2 mmol), **2** (2 mmol), TEBAC (20 mol %), water (10 mL), 50 °C.
[b] Isolated yields.



1 **5** **6**

Scheme 4.

Table 5. TEBAC catalyzed reaction of **1** and **5** in the absence of K_2CO_3[a]

Entry	Ar	Ar′	Time/h	Yields[b]/%
6a	4-BrC_6H_4	4-ClC_6H_4	12	90
6b	4-$CH_3C_6H_4$	4-ClC_6H_4	12	86
6c	4-$CH_3OC_6H_4$	2,4-Cl_2-5-FC_6H_2	14	82
6d	2-ClC_6H_4	2,4-Cl_2-5-FC_6H_2	12	83
6e	3,4-$Cl_2C_6H_3$	2,4-$(CH_3)_2C_6H_3$	14	84
6f	4-ClC_6H_4	2,4-$(CH_3)_2C_6H_3$	16	84
6g	4-ClC_6H_4	4-$CH_3C_6H_4$	14	91
6h	3,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	14	90
6i	2-ClC_6H_4	4-$CH_3C_6H_4$	12	94
6j	4-Cl-2-$NO_2C_6H_3$	4-$CH_3C_6H_4$	10	95
6k	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	14	86
6l	3-ClC_6H_4	4-$CH_3C_6H_4$	12	91
6m	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	14	90

[a] Reagents and conditions: **1** (2 mmol), **5** (2 mmol), TEBAC (20 mol %), water (10 mL), 50 °C.
[b] Isolated yields.

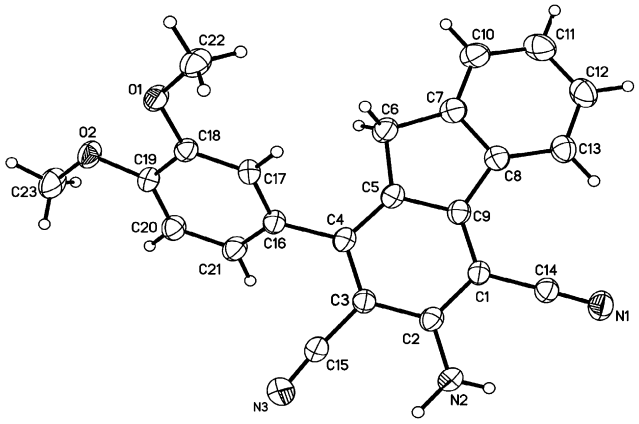


Figure 1. The crystal structure of the product **3m**.

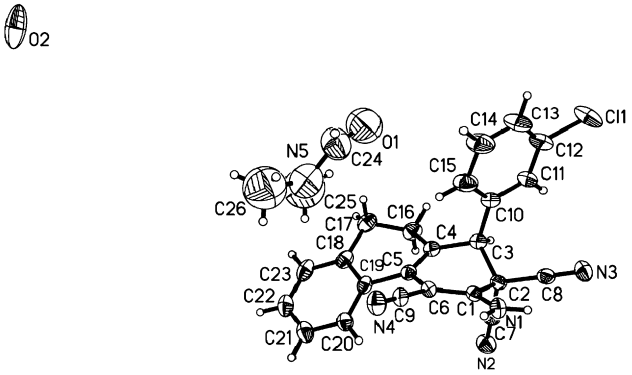


Figure 2. The crystal structure of the product **4b** semi-dimethylformamide and semi-hydrate.

The structures of **3**, **4** and **6** were characterized by ^1H NMR, ^{13}C NMR, IR and elemental analysis, and the structures of **3m** and **4b** were additionally confirmed by X-ray diffraction analysis.[10] The crystal structure of **3m** and **4b** are shown in Figures 1 and 2, respectively.

3. Conclusion

In conclusion, an efficient method for the synthesis of the one-donor poly-acceptors systems containing 2,6-dicyanoamine moiety by condensation of 1-arylethylidenemalonodinitriles with arylidenemalonodinitriles was successfully established in aqueous media catalyzed by TEBAC in the presence of K_2CO_3. The important intermediates containing one donor and three acceptors were obtained successfully to confirm the mechanism in the absence of base under the same reaction conditions. The advantages of this procedure are high yields, mild reaction conditions, easy work-up, inexpensive reagents and environmentally friendly procedure.

4. Experimental

4.1. General

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr pellet. ^1H NMR spectra were obtained in DMSO-d_6 or $CDCl_3$ solution with Me_4Si as internal standard using a Bruker-400 spectrometer. Elemental analyses were carried out using Perkin–Elmer 240 II analyzer. X-ray diffraction was measured on a Rigaku Mercury or CCD area diffractometer.

4.2. General procedure for the syntheses of 3-amino-1-aryl-2,4-dicyano-9,10-dihydrophenanthrene (3)

A suspension of arylidenemalonodinitriles **1** (2 mmol), 2-(2,3-dihydronaphthalen-4(1*H*)ylidene) malononitrile or 2-(2,3-dihydroinden-3-ylidene) malononitrile **2** (2 mmol), K_2CO_3 (0.276 g, 4 mmol) and TEBAC (0.091 g, 0.4 mmol) was stirred in water (10 mL) at 50 °C for 8–14 h. The precipitated product was collected by filtration, washed with water and recrystallized from 95% EtOH to give **3**.

4.2.1. 3-Amino-1-(4-chlorophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3a). Pale yellow crystals; mp 238–240 °C. IR (KBr): 3439, 3353, 3243, 3089, 2945, 2884, 2835, 2210, 1639, 1596, 1352, 1494, 1431, 1396, 1353, 1287, 1265, 1221, 1155, 1090, 1016, 913, 823, 765, 748. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.27–2.30 (m, 2H, CH_2), 2.62–2.65 (m, 2H, CH_2), 6.63 (s, 2H, NH_2), 7.36–7.38 (m, 1H, ArH), 7.41–7.45 (m, 4H, ArH), 7.61 (d, J=8.0 Hz, 2H, ArH), 8.14–8.16 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.0, 28.7, 92.7, 96.3, 116.4, 117.7, 126.3, 127.1, 127.7, 128.4, 129.2, 130.8, 131.2, 131.3, 134.2, 136.3, 140.5, 143.0, 147.6, 153.2. Anal. Calcd for $C_{22}H_{14}ClN_3$: C, 74.26; H, 3.97; N, 11.81. Found: C, 74.10; H, 4.20; N, 11.78.

4.2.2. 3-Amino-1-(4-fluorophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3b). Pale yellow crystals; mp 237–239 °C. IR (KBr): 3468, 3370, 3246, 2946, 2902, 2842, 2208, 1638, 1604, 1555, 1512, 1432, 1352, 1286, 1266, 1222, 1157, 1098, 1019, 913, 860, 832, 790, 768, 751, 727. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.28–2.31 (m, 2H, CH_2), 2.62–2.65 (m, 2H, CH_2), 6.60 (s, 2H, NH_2), 7.36–7.48 (m, 7H, ArH), 8.14–8.16 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.0, 28.8, 92.6, 96.6, 116.0, 116.2, 116.4, 117.7, 126.6, 127.1, 127.6, 128.4, 130.8, 131.4, 131.5, 131.6, 133.7, 140.4, 142.9, 147.9, 153.1. Anal. Calcd for $C_{22}H_{14}FN_3$: C, 77.86; H, 4.16; N, 12.38. Found: C, 77.98; H, 4.20; N, 12.21.

4.2.3. 3-Amino-1-(2-chlorophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3c). Pale yellow crystals; mp 229–231 °C. IR (KBr): 3472, 3368, 3236, 3072, 2957, 2844, 2214, 1673, 1632, 1557, 1478, 1433, 1289, 1267, 1221, 1158, 1060, 1030, 912, 773, 752, 697. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.16–2.18 (m, 2H, CH_2), 2.64–2.69 (m, 2H, CH_2), 6.68 (s, 2H, NH_2), 7.36–7.38 (m, 1H, ArH), 7.43–7.57 (m, 6H, ArH), 7.68 (d, J=8.0 Hz, 1H, ArH), 8.18–8.20 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.6, 28.7, 93.0, 96.5, 115.8, 117.6, 126.0, 127.2, 127.7, 128.3, 128.5, 130.1, 130.9, 131.1, 131.2, 131.3, 132.2, 136.2, 140.5, 142.9, 146.0, 153.1. Anal. Calcd for $C_{22}H_{14}ClN_3$: C, 74.26; H, 3.97; N, 11.81. Found: C, 74.50; H, 3.77; N, 11.69.

4.2.4. 3-Amino-1-(3-chlorophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3d). Pale yellow crystals; mp 218–220 °C. IR (KBr): 3459, 3349, 3236, 3064, 2951, 2894, 2838, 2214, 1638, 1553, 1479, 1432, 1324, 1286, 1265, 1218, 1155, 1093, 1080, 892, 795, 764, 724, 705. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26–2.29 (m, 2H, CH_2), 2.62–2.65 (m, 2H, CH_2), 6.60 (s, 2H, NH_2), 7.35–7.37 (m, 2H, ArH), 7.42–7.74 (m, 2H, ArH), 7.50 (s, 1H, ArH), 7.56–7.57 (m, 2H, ArH), 8.13–8.15 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.0, 28.8, 92.8, 96.3, 116.2, 117.6, 126.3, 127.1, 127.6, 128.0, 128.4, 128.9, 129.3, 130.8, 131.1, 131.3, 133.8, 139.5, 140.4, 143.0, 147.2, 153.1. Anal. Calcd for $C_{22}H_{14}ClN_3$: C, 74.26; H, 3.97; N, 11.81. Found: C, 74.39; H, 3.90; N, 11.86.

4.2.5. 3-Amino-1-(4-methylphenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3e). Pale yellow crystals; mp 197–199 °C. IR (KBr): 3455, 3357, 3243, 3016, 2955, 2905, 2842, 2217, 2203, 1639, 1552, 1515, 1488, 1458, 1430, 1285, 1264, 1222, 1210, 1180, 1162, 814, 768, 749, 669. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.28–2.32 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.60–2.63 (m, 2H, CH_2), 6.55 (s, 2H, NH_2), 7.27 (d, J=8.0 Hz, 2H, ArH), 7.34 (d, J=8.0 Hz, 2H, ArH), 7.36–7.37 (m, 1H, ArH), 7.42–7.44 (m, 2H, ArH), 8.13–8.16 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.4, 26.1, 28.8, 92.3, 96.6, 116.5, 117.8, 126.5, 127.0, 127.6, 128.4, 129.1, 129.7, 130.7, 131.5, 134.5, 138.8, 140.5, 142.8, 149.0, 153.1. Anal. Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.11; N, 12.53. Found: C, 82.20; H, 5.32; N, 12.67.

4.2.6. 3-Amino-1-(4-bromophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3f). Pale yellow crystals; mp 253–255 °C. IR (KBr): 3437, 3353, 3242, 3086, 2944, 2884, 2833, 2210, 1639, 1591, 1551, 1491, 1430, 1392, 1287, 1264, 1220, 1154, 1072, 1012, 911, 820, 764, 746. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.26–2.29 (m, 2H, CH_2), 2.61–2.64 (m, 2H, CH_2), 6.59 (s, 2H, NH_2), 7.36 (d, J=8.0 Hz, 3H, ArH), 7.43 (t, J=7.6 Hz, 2H, ArH), 7.74 (d, J=8.4 Hz, 2H, ArH), 8.13–8.16 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.0, 28.8, 92.7, 96.3, 116.3, 117.7, 122.9, 126.3, 127.1, 127.7, 128.4, 130.8, 131.37, 131.44, 132.1, 136.7, 140.5, 143.1, 145.6, 153.1. Anal. Calcd for $C_{22}H_{14}BrN_3$: C, 66.01; H, 3.53; N, 10.50. Found: C, 66.24; H, 3.44; N, 10.40.

4.2.7. 3-Amino-1-(3,4-dichlorophenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3g). Pale yellow crystals; mp 155–156 °C. IR (KBr): 3468, 3362, 3241, 2956, 2218, 1638, 1561, 1481, 1432, 1290, 1265, 1218, 1099, 915, 826, 816, 749. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.31 (t, 2H, J=6.4 Hz, CH_2), 2.65 (t, 2H, J=6.4 Hz, CH_2), 6.68 (s, 2H, NH_2), 7.37–7.48 (m, 4H, ArH), 7.78 (d, 1H, J=2.0 Hz, ArH), 7.82 (d, 1H, J=8.0 Hz, ArH), 8.14–8.16 (m, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.6, 28.7, 93.3, 96.3, 115.8, 117.5, 126.6, 127.2, 127.7, 128.55, 128.58, 129.7, 130.9, 131.1, 132.5, 133.4, 135.20, 135.23, 140.5, 143.1, 144.8, 153.2. Anal. Calcd for $C_{22}H_{13}Cl_2N_3$: C, 67.71; H, 3.36; N, 10.77. Found: C, 67.66; H, 3.40; N, 10.73.

4.2.8. 3-Amino-1-(3,4-dimethoxyphenyl)-2,4-dicyano-9,10-dihydrophenanthrene (3h). Pale yellow crystals; mp 266–268 °C. IR (KBr): 3472, 3398, 2949, 2210, 1673, 1616, 1553, 1515, 1433, 1252, 1137, 1015, 807, 761, 747. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.34–2.42 (m, 2H, CH_2), 2.59–2.64 (m, 2H, CH_2), 3.75 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 6.53 (s, 2H, NH_2), 6.98 (d, 1H, J=1.6 Hz, ArH), 7.09 (d, 1H, J=8.4 Hz, ArH), 7.36–7.44 (m, 3H, ArH), 8.12–8.14 (m, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.2, 28.9, 56.0, 56.2, 92.1, 96.8, 112.1, 113.1, 116.6, 117.8, 121.8, 126.8, 127.0, 127.6, 128.4, 129.6, 130.6, 131.6, 140.5, 142.8, 149.0, 149.6, 153.1. Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.68; H, 5.14; N 10.88.

4.2.9. 3-Amino-1-(2,4-dichlorophenyl)-2,4-dicyano-9*H*-fluorene (3i). Pale yellow crystals; mp 267–269 °C. IR (KBr): 3469, 3364, 3244, 2218, 1716, 1639, 1574, 1561, 1488, 1446, 1381, 1308, 1264, 1102, 802, 752, 719. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.58 (s, 2H, CH_2), 6.92 (s, 2H, NH_2), 7.53–7.65 (m, 5H, ArH), 7.93 (d, 1H, J=2.0 Hz, ArH), 8.36 (d, 1H, J=7.2 Hz, ArH). ^{13}C NMR

(100 MHz, DMSO-d_6): δ 35.2, 88.7, 95.2, 116.0, 122.6, 126.2, 128.1, 128.55, 128.57, 129.9, 130.5, 131.1, 132.4, 133.1, 134.6, 135.3, 137.9, 143.1, 146.4, 147.5, 153.7. Anal. Calcd for $C_{21}H_{11}Cl_2N_3$: C, 67.04; H, 2.95; N, 11.17. Found: C, 66.89; H, 3.12; N, 11.00.

4.2.10. 3-Amino-1-(4-bromophenyl)-2,4-dicyano-9*H*-fluorene (3j). Pale yellow crystals; mp 257–259 °C. IR (KBr): 3450, 3359, 3236, 2211, 1038, 1568, 1493, 1476, 1447, 1420, 1377, 1305, 1205, 1156, 1076, 1011, 831, 753, 724. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.66 (s, 2H, CH_2), 6.76 (s, 2H, NH_2), 7.50–7.55 (m, 4H, ArH), 7.61 (d, J=6.4 Hz, 1H, ArH), 7.77 (d, J=8.4 Hz, 1H, ArH), 8.32 (d, J=7.6 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.6, 88.0, 94.6, 116.2, 116.6, 122.4, 123.2, 125.9, 127.8, 130.3, 130.8, 131.3, 132.2, 136.0, 137.9, 145.6, 146.6, 147.2, 153.9. Anal. Calcd for $C_{21}H_{12}BrN_3$: C, 65.30; H, 3.13; N, 10.88. Found: C, 65.42; H, 3.20; N, 10.73.

4.2.11. 3-Amino-1-(4-fluorophenyl)-2,4-dicyano-9*H*-fluorene (3k). Pale yellow crystals; mp 264–266 °C. IR (KBr): 3456, 3363, 3250, 2203, 1640, 1601, 1561, 1521, 1476, 1449, 1396, 1375, 1303, 1266, 1227, 1203, 1155, 1098, 843, 755, 723. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.69 (s, 2H, CH_2), 6.78 (s, 2H, NH_2), 7.41 (t, J=8.8 Hz, 2H, ArH), 7.50–7.56 (m, 2H, ArH), 7.63–7.68 (m, 3H, ArH), 8.34 (d, J=6.8 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.7, 87.8, 94.9, 116.1, 116.3, 116.7, 122.4, 126.0, 127.9, 130.2, 130.3, 131.0, 131.5, 131.6, 133.2, 138.0, 145.9, 146.7, 147.2, 154.0. Anal. Calcd for $C_{21}H_{12}FN_3$: C, 77.53; H, 3.72; N, 12.92. Found: C, 77.40; H, 3.77; N, 12.85.

4.2.12. 3-Amino-1-(4-chlorophenyl)-2,4-dicyano-9*H*-fluorene (3l). Pale yellow crystals; mp 275–277 °C. IR (KBr): 3453, 3362, 3237, 2209, 1634, 1593, 1559, 1495, 1475, 1396, 1375, 1304, 1265, 1093, 1014, 834, 754, 725. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.69 (s, 2H, CH_2), 6.80 (s, 2H, NH_2), 7.52–7.58 (m, 2H, ArH), 7.61–7.63 (m, 5H, ArH), 8.35 (d, J=7.2 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.7, 88.0, 94.7, 116.2, 116.6, 112.5, 126.1, 127.9, 129.3, 130.3, 130.9, 131.1, 134.5, 135.7, 138.0, 145.7, 146.7, 147.3, 154.0. Anal. Calcd for $C_{21}H_{12}ClN_3$: C, 73.79; H, 3.54; N, 12.29. Found: C, 73.94; H, 3.50; N, 12.43.

4.2.13. 3-Amino-1-(3,4-dimethoxyphenyl)-2,4-dicyano-9*H*-fluorene (3m). Pale yellow crystals; mp 252–254 °C. IR (KBr): 3459, 3363, 2936, 2213, 1640, 1568, 1519, 1465, 1439, 1258, 1138, 1024, 813, 758. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.76 (s, 2H, CH_2), 3.81 (s, 3H, CH_3O), 3.85 (s, 3H, CH_3O), 6.65 (s, 2H, NH_2), 7.13 (s, 2H, ArH), 7.19 (s, 1H, ArH), 7.50–7.56 (m, 2H, ArH), 7.64 (d, 1H, J=7.2 Hz, ArH), 8.35 (d, 1H, J=7.2 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 36.0, 56.0, 56.2, 87.3, 95.6, 112.2, 112.9, 116.4, 117.0, 121.8, 122.3, 126.0, 126.3, 127.8, 129.1, 130.1, 131.1, 138.1, 146.7, 146.9, 149.0, 149.9, 154.0. Anal. Calcd for $C_{23}H_{17}N_3O_2$: C, 75.19; H, 4.66; N, 11.44. Found: C, 75.00; H, 4.75; N, 11.43.

4.2.14. 3-Amino-1-(4-nitrophenyl)-2,4-dicyano-9*H*-fluorene (3n). Pale yellow crystals; mp 261–263 °C. IR (KBr): 3467, 3372, 3355, 3242, 2213, 1639, 1564, 1472, 1447, 1305, 1030, 836, 755. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.70 (s, 2H, CH_2), 6.78 (s, 2H, NH_2), 7.39–7.44 (m, 2H, ArH), 7.52–7.55 (m, 2H, ArH), 7.64–7.68 (m, 3H, ArH), 8.35 (d, 1H, J=7.2 Hz, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.6, 88.5, 94.3, 116.1, 116.4, 122.5, 124.3, 126.1, 128.0, 130.5, 130.7, 130.9, 137.9, 143.4, 144.7, 146.7, 147.6, 148.3, 153.9. Anal. Calcd for $C_{21}H_{12}N_4O_2$: C, 71.58; H, 3.43; N, 15.90. Found: C, 71.50; H, 3.52; N 15.83.

4.2.15. 3-Amino-1-(3,4-dichlorophenyl)-2,4-dicyano-9*H*-fluorene (3o). Pale yellow crystals; mp 211–214 °C. IR (KBr): 3042, 2216, 1635, 1617, 1605, 1532, 1473, 1415, 1404, 1335, 1313, 1213, 1162, 1137, 1104, 1023, 910, 816, 774, 729. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.15 (s, 2H, CH_2), 7.57–7.60 (m, 1H, ArH), 7.66–7.75 (m, 3H, ArH), 7.80 (d, J=8.4 Hz, 1H, ArH), 7.98 (d, J=2.0 Hz, 1H, ArH), 8.10 (s, 2H, NH_2), 8.38 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 35.3, 88.0, 94.3, 115.8, 122.2, 125.7, 127.6, 129.4, 130.1, 130.6, 130.9, 131.1, 131.7, 132.2, 137.1, 137.6, 143.8, 146.4, 147.1, 153.6. Anal. Calcd for $C_{21}H_{11}Cl_2N_3$: C, 67.04; H, 2.95; N, 11.17. Found: C, 67.26; H, 2.77; N, 11.10.

4.3. General procedure for the syntheses of 3-amino-1-aryl-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene 4

A suspension of arylidenemalonodinitriles **1** (2 mmol), 2-(2,3-dihydronaphthalen-4(1*H*)ylidene) malononitrile or 2-(2,3-dihydroinden-3-ylidene) malononitrile **2** (2 mmol) and TEBAC (0.091 g, 0.4 mmol) was stirred in water (10 mL) at 50 °C for 6–10 h. The precipitated product was collected by filtration, washed with water and recrystallized from 95% EtOH or DMF and H_2O, followed by keeping at 50 °C for 5 h under *vacuum* to give pure immediate products **4**.

4.3.1. 3-Amino-1-(4-chlorophenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4a). Pale yellow crystals; mp 233–235 °C. IR (KBr): 3415, 3325, 3239, 3097, 3058, 2949, 2913, 2883, 2820, 2206, 1652, 1582, 1490, 1423, 1409, 1389, 1229, 1207, 1093, 1012, 936, 842, 801, 775, 767, 741. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.97–2.08 (m, 1H, CH), 2.20–2.29 (m, 1H, CH), 2.47–2.57 (m, 1H, CH), 2.64–2.68 (m, 1H, CH), 4.76 (s, 1H, CH), 7.22–7.32 (m, 3H, ArH), 7.44 (d, J=8.0 Hz, 2H, ArH), 7.50–7.52 (m, 3H, ArH), 7.59 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.0, 28.6, 42.3, 49.7, 75.7, 111.8, 113.8, 117.7, 124.6, 126.7, 126.8, 126.9, 128.2, 128.3, 129.4, 131.2, 132.0, 132.3, 134.8, 136.8, 147.3. Anal. Calcd for $C_{23}H_{15}ClN_4$: C, 72.16; H, 3.95; N, 14.63. Found: C, 72.20; H, 3.88; N, 14.69.

4.3.2. 3-Amino-1-(3-chlorophenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4b). Pale yellow crystals; mp 149–151 °C. IR (KBr): 3392, 3257, 3071, 2915, 2218, 1612, 1597, 1572, 1556, 1477, 1436, 1425, 1382, 1336, 1309, 1227, 1201, 1160, 893, 875, 806, 784, 757, 738, 718, 693. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.01–2.06 (m, 1H, CH), 2.22–2.31 (m, 1H, CH), 2.54–2.59 (m, 1H, CH), 2.66–2.71 (m, 1H, CH), 4.83 (s, 1H, CH), 7.24–7.34 (m, 3H, ArH), 7.39 (d, J=7.6 Hz, 1H, ArH), 7.47–7.52 (m, 4H, ArH), 7.65 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.0, 28.6, 42.3, 49.8, 75.6,

111.7, 113.7, 117.6, 124.6, 126.6, 126.9, 128.3, 128.4, 128.6, 130.0, 130.1, 131.1, 131.4, 133.8, 135.8, 136.8, 147.4. Anal. Calcd for $C_{23}H_{15}ClN_4$: C, 72.16; H, 3.95; N, 14.63. Found: C, 72.34; H, 3.89; N, 14.52.

4.3.3. 3-Amino-1-(4-methoxyphenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4c). Pale yellow crystals; mp 230–232 °C. IR (KBr): 3390, 3268, 3068, 2956, 2837, 2215, 1612, 1572, 1555, 1515, 1456, 1379, 1336, 1308, 1293, 1256, 1180, 1061, 1028, 891, 835, 778, 731. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.97–2.02 (m, 1H, CH), 2.25–2.32 (m, 1H, CH), 2.53–2.57 (m, 1H, CH), 2.65–2.69 (m, 1H, CH), 3.37 (s, 3H, CH_3O), 4.46 (s, 1H, CH), 6.99 (d, J=8.8 Hz, 2H, ArH), 7.24–7.31 (m, 3H, ArH), 7.34 (d, J=8.4 Hz, 2H, ArH), 7.50 (d, J=7.6 Hz, 1H, ArH), 7.54 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.7, 28.3, 48.1, 48.4, 55.4, 101.1, 112.3, 112.4, 114.7, 115.5, 126.5, 126.9, 128.7, 128.8, 129.7, 129.9, 130.3, 133.6, 141.7, 158.3, 160.1, 164.5. Anal. Calcd for $C_{24}H_{18}N_4O$: C, 76.17; H, 4.79; N, 14.81. Found: C, 75.98; H, 4.96; N, 14.72.

4.3.4. 3-Amino-1-(4-bromophenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4d). Pale yellow crystals; mp 214–216 °C. IR (KBr): 3348, 3325, 3242, 3057, 2950, 2927, 2912, 2884, 2819, 2207, 1653, 1625, 1603, 1583, 1508, 1487, 1424, 1361, 1230, 1207, 1161, 1106, 856, 843, 804, 775, 767, 740. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.98–2.03 (m, 1H, CH), 2.21–2.31 (m, 1H, CH), 2.54–2.59 (m, 1H, CH), 2.65–2.69 (m, 1H, CH), 4.79 (s, 1H, CH), 7.25–7.32 (m, 3H, ArH), 7.38 (d, J=8.4 Hz, 2H, ArH), 7.51 (d, J=7.6 Hz, 1H, ArH), 7.60 (s, 2H, NH_2), 7.66 (d, J=8.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.9, 28.6, 42.2, 49.8, 75.7, 111.8, 113.8, 117.7, 123.5, 124.6, 126.7, 126.9, 128.2, 128.3, 131.2, 132.3, 132.4, 132.7, 134.5, 136.8, 147.3. Anal. Calcd for $C_{23}H_{15}BrN_4$: C, 64.65; H, 3.54; N, 13.11. Found: C, 64.79; H, 3.50; N, 13.01.

4.3.5. 3-Amino-1-(3-nitrophenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4e). Pale yellow crystals; mp 213–215 °C. IR (KBr): 3348, 3257, 3099, 3078, 2924, 2867, 2219, 1614, 1571, 1556, 1536, 1481, 1451, 1431, 1384, 1346, 1160, 1083, 1060, 899, 835, 804, 776, 735, 725. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.02–2.07 (m, 1H, CH), 2.24–2.33 (m, 1H, CH), 2.56–2.61 (m, 1H, CH), 2.66–2.70 (m, 1H, CH), 5.05 (s, 1H, CH), 7.25–7.36 (m, 3H, ArH), 7.54 (d, J=7.6 Hz, 1H, ArH), 7.67 (s, 2H, NH_2), 7.76–7.80 (m, 1H, ArH), 7.88 (d, J=8.0 Hz, 1H, ArH), 8.31–8.33 (m, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 27.8, 28.7, 42.2, 47.8, 75.8, 101.3, 112.3, 115.0, 125.0, 126.9, 127.4, 129.2, 130.0, 130.1, 131.4, 134.0, 137.2, 141.9, 147.2, 148.2, 148.0, 157.9, 164.4. Anal. Calcd for $C_{23}H_{15}N_5O_2$: C, 70.22; H, 3.84; N, 17.80. Found: C, 70.02; H, 3.88; N, 17.69.

4.3.6. 3-Amino-1-(2,4-dichlorophenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4f). Pale yellow crystals; mp 215–217 °C. IR (KBr): 3445, 3334, 3243, 3201, 3078, 3028, 2952, 2925, 2897, 2835, 2204, 1636, 1583, 1558, 1488, 1468, 1385, 1362, 1232, 1209, 1187, 1144, 1102, 1051, 881, 854, 799, 777, 741. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.91–1.96 (m, 1H, CH), 2.25–2.34 (m, 1H, CH), 2.46–2.55 (m, 1H, CH), 2.64–2.69 (m, 1H, CH), 4.90 (s, 1H, CH), 7.23–7.34 (m, 3H, ArH), 7.39 (d, J=8.4 Hz, 1H, ArH), 7.53–7.57 (m, 2H, ArH), 7.75 (s, 2H, NH_2), 7.86 (d, J=2.4 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.9, 28.6, 40.0, 47.0, 76.0, 111.2, 113.3, 117.5, 124.7, 125.9, 126.9, 127.2, 128.2, 128.5, 129.3, 130.1, 130.4, 131.0, 131.5, 135.8, 136.3, 136.8, 146.8. Anal. Calcd for $C_{23}H_{14}Cl_2N_4$: C, 66.20; H, 3.38; N, 13.43. Found: C, 66.24; H, 3.19; N, 13.56.

4.3.7. 3-Amino-1-(3,4-dimethylphenyl)-2,2,4-tricyano-1,2,9,10-tetrahydrophenanthrene (4g). Pale yellow crystals; mp 224–226 °C. IR (KBr): 3430, 3331, 3234, 3196, 3099, 3067, 3021, 2949, 2926, 2854, 2837, 2203, 1634, 1576, 1498, 1488, 1454, 1435, 1394, 1360, 1229, 1197, 1107, 1023, 800, 775, 767, 738. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.97–2.04 (m, 1H, CH), 2.21 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.23–2.29 (m, 1H, CH), 2.48–2.57 (m, 1H, CH), 2.63–2.74 (m, 1H, CH), 4.62 (s, 1H, CH), 7.12–7.19 (m, 3H, ArH), 7.23–7.34 (m, 3H, ArH), 7.50 (d, J=7.6 Hz, 1H, ArH), 7.54 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.6, 20.1, 27.0, 28.7, 42.6, 50.6, 75.6, 112.0, 114.0, 117.8, 124.5, 126.3, 126.9, 127.4, 127.6, 128.1, 128.2, 130.4, 130.6, 131.2, 131.4, 136.7, 137.7, 138.2, 147.5. Anal. Calcd for $C_{25}H_{20}N_4$: C, 79.76; H, 5.35; N, 14.88. Found: C, 79.89; H, 5.24; N, 14.70.

4.3.8. 3-Amino-1-(4-fluorophenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4h). Pale yellow crystals; mp 199–201 °C. IR (KBr): 3387, 3282, 3052, 2214, 1620, 1606, 1594, 1575, 1513, 1469, 1436, 1362, 1341, 1300, 1224, 1164, 1118, 849, 825, 804, 774, 757. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.35 (s, 2H, CH_2), 5.22 (s, 1H, CH), 7.26–7.31 (m, 3H, ArH), 7.37–7.41 (m, 1H, ArH), 7.45–7.49 (m, 3H, ArH), 7.89 (d, J=8.0 Hz, 1H, ArH), 8.00 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.3, 44.0, 48.0, 72.0, 112.2, 113.5, 116.3, 116.5, 117.2, 119.4, 124.8, 126.1, 127.1, 129.3, 131.3, 132.05, 132.14, 140.4, 144.0, 147.9, 161.8. Anal. Calcd for $C_{22}H_{13}FN_4$: C, 74.99; H, 3.72; N, 15.90. Found: C, 75.20; H, 3.50; N, 15.79.

4.3.9. 3-Amino-1-(3,4-dichlorophenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4i). Pale yellow crystals; mp 191–193 °C. IR (KBr): 3432, 3306, 3203, 3092, 3068, 2219, 1648, 1598, 1575, 1471, 1400, 1199, 1133, 1031, 873, 843, 771, 752, 721, 667. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.38 (s, 2H, CH_2), 5.28 (s, 1H, CH), 7.27–7.31 (m, 1H, ArH), 7.35–7.41 (m, 2H, ArH), 7.48 (d, J=7.6 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.73 (d, J=8.4 Hz, 1H, ArH), 7.89 (d, J=8.0 Hz, 1H, ArH), 8.07 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.3, 43.6, 47.4, 72.6, 112.0, 113.3, 117.0, 119.5, 124.9, 126.3, 127.1, 128.2, 129.8, 131.7, 131.8, 131.9, 132.0, 132.8, 135.3, 140.2, 144.1, 147.6. Anal. Calcd for $C_{22}H_{12}Cl_2N_4$: C, 65.52; H, 3.00; N, 13.89. Found: C, 65.70; H, 3.18; N, 13.71.

4.3.10. 3-Amino-1-(2,4-dichlorophenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4j). Pale yellow crystals; mp 194–196 °C. IR (KBr): 3444, 3310, 3224, 3205, 3073, 2887, 2212, 1645, 1598, 1576, 1472, 1391, 1245, 1197, 1103, 1081, 1049, 933, 846, 822, 766, 720. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.30 (d, J=36.4 Hz, 1H, CH), 3.46 (d, J=36.4 Hz, 1H, CH), 5.46 (s, 1H, CH), 7.27–7.31

(m, 1H, ArH), 7.37–7.41 (m, 2H, ArH), 7.47 (d, J=7.6 Hz, 1H, ArH), 7.52 (dd, J=2.0 Hz, J'=8.4 Hz, 1H, ArH), 7.85 (d, J=2.0 Hz, 1H, ArH), 7.91 (d, J=7.6 Hz, 1H, ArH), 8.12 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.3, 42.4, 44.8, 72.8, 111.7, 113.0, 117.0, 119.5, 124.8, 126.3, 127.1, 127.8, 129.1, 130.2, 131.2, 131.5, 131.8, 135.49, 135.53, 140.1, 144.1, 147.3. Anal. Calcd for $C_{22}H_{12}Cl_2N_4$: C, 65.52; H, 3.00; N, 13.89. Found: C, 65.69; H, 3.22; N, 13.84.

4.3.11. 3-Amino-1-(4-chlorophenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4k). Pale yellow crystals; mp 207–209 °C. IR (KBr): 3414, 3330, 3242, 3073, 3026, 2203, 1650, 1595, 1572, 1493, 1466, 1413, 1376, 1278, 1250, 1198, 1089, 1013, 933, 839, 767, 750, 740, 717. ^1H NMR (400 MHz, DMSO-d_6): δ 3.35 (s, 2H, CH_2), 5.24 (s, 1H, CH), 7.26–7.29 (m, 1H, ArH), 7.37–7.40 (m, 1H, ArH), 7.43–7.48 (m, 3H, ArH), 7.52 (d, J=8.4 Hz, 2H, ArH), 7.90 (d, J=7.6 Hz, 1H, ArH), 8.03 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.3, 43.8, 48.0, 72.7, 112.1, 113.5, 117.1, 119.5, 124.8, 126.2, 127.1, 128.9, 129.5, 131.5, 131.7, 133.3, 134.6, 140.3, 144.0, 147.8. Anal. Calcd for $C_{22}H_{13}ClN_4$: C, 71.64; H, 3.55; N, 15.19. Found: C, 71.50; H, 3.44; N, 15.42.

4.3.12. 3-Amino-1-(2-methoxyphenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4l). Pale yellow crystals; mp 185–188 °C. IR (KBr): 3432, 3317, 3233, 3208, 2960, 2935, 2837, 2211, 1647, 1584, 1521, 1490, 1461, 1437, 1388, 1341, 1311, 1288, 1246, 1160, 1106, 1051, 1028, 753, 725. ^1H NMR (400 MHz, DMSO-d_6): δ 3.24 (d, J=36.4 Hz, 1H, CH), 3.45 (d, J=36.4 Hz, 1H, CH), 3.86 (s, 3H, CH_3O), 5.33 (s, 1H, CH), 6.96–7.00 (m, 1H, ArH), 7.14–7.17 (m, 2H, ArH), 7.27 (d, J=7.2 Hz, 1H, ArH), 7.38–7.41 (m, 2H, ArH), 7.45 (d, J=7.2 Hz, 1H, ArH), 7.88 (d, J=8.0 Hz, 1H, ArH), 7.95 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.3, 42.7, 56.1, 72.5, 112.2, 112.4, 113.8, 117.3, 119.3, 121.2, 121.4, 122.2, 124.7, 126.0, 126.4, 127.0, 129.0, 129.3, 131.2, 140.5, 143.9, 147.9, 157.5. Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.38. Found: C, 75.57; H, 4.54; N, 15.59.

4.3.13. 3-Amino-1-(2-nitrophenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4m). Pale yellow crystals; mp 193–195 °C. IR (KBr): 3410, 3256, 2957, 2216, 1619, 1589, 1674, 1524, 1465, 1434, 1344, 1317, 1280, 1221, 1192, 1158, 1125, 1076, 1048, 959, 896, 857, 778, 752, 725, 711. ^1H NMR (400 MHz, DMSO-d_6): δ 3.27 (d, J=36.4 Hz, 1H, CH), 3.54 (d, J=36.4 Hz, 1H, CH), 5.73 (s, 1H, CH), 7.29 (t, J=7.2 Hz, 1H, ArH), 7.40 (t, J=7.6 Hz, 1H, ArH), 7.46–7.51 (m, 2H, ArH), 7.69–7.72 (m, 1H, ArH), 7.79 (t, J=7.6 Hz, 1H, ArH), 7.93 (d, J=7.6 Hz, 1H, ArH), 8.11 (s, 2H, NH_2), 8.16 (d, J=8.0 Hz, 1H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.6, 42.5, 43.5, 72.7, 112.0, 113.4, 117.0, 119.6, 124.8, 126.2, 126.3, 127.1, 127.9, 129.5, 130.4, 131.41, 131.44, 135.2, 140.1, 144.2, 147.4, 149.4. Anal. Calcd for $C_{22}H_{13}N_5O_2$: C, 69.65; H, 3.45; N, 18.46. Found: C, 69.70; H, 3.53; N, 18.32.

4.3.14. 3-Amino-1-(4-methylphenyl)-2,2,4-tricyano-1,2-dihydro-9*H*-fluorene (4n). Pale yellow crystals; mp 191–193 °C. IR (KBr): 3410, 3334, 3245, 3028, 2920, 2880, 2202, 1653, 1601, 1573, 1515, 1467, 1377, 1279, 1197, 1025, 933, 827, 764, 745, 716. ^1H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, CH_3), 3.32 (s, 2H, CH_2), 5.11 (s, 1H, CH), 7.23–7.27 (m, 3H, ArH), 7.30 (d, J=7.6 Hz, 2H, ArH), 7.38 (t, J=7.6 Hz, 1H, ArH), 7.46 (d, J=7.2 Hz, 1H, ArH), 7.88 (d, J=8.0 Hz, 1H, ArH), 7.97 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 38.4, 44.1, 48.7, 72.6, 112.3, 113.6, 117.3, 119.4, 124.8, 126.0, 127.1, 129.68, 129.72, 130.0, 131.2, 131.3, 139.3, 140.5, 144.0, 148.1. Anal. Calcd for $C_{23}H_{16}N_4$: C, 79.29; H, 4.63; N, 16.08. Found: C, 79.11; H, 4.54; N, 16.23.

4.4. General procedure for the syntheses of 2-amino-4,6-diaryl-cyclohexa-2,4-diene-1,1,3-tricarbonitrile 6

A suspension of arylidenemalonodinitriles **1** (2 mmol), 1-arylethylidenemalonodinitriles **5** (2 mmol) and TEBAC (0.091 g, 0.4 mmol) was stirred in water (10 mL) at 50 °C for 10–16 h. The precipitated product was collected by filtration, washed with water and recrystallized from 95% EtOH to give **6**.

4.4.1. 2-Amino-4-(4-chlorophenyl)-6-(4-bromophenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6a). Pale yellow crystals; mp 236–238 °C. IR (KBr): 3396, 3306, 3208, 2216, 1642, 1608, 1552, 1488, 1401, 1325, 1091, 1071, 1009, 817. ^1H NMR (400 MHz, DMSO-d_6): δ 6.62 (d, J=16.0 Hz, 1H, CH), 7.28 (d, J=15.6 Hz, 1H, CH), 7.40 (d, J=8.0 Hz, 2H, ArH), 7.60 (d, J=8.8 Hz, 2H, ArH), 7.63 (d, J=8.8 Hz, 2H, ArH), 7.69 (d, J=8.0 Hz, 2H, ArH), 9.24 (s, 1H, NH), 9.39 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.5, 103.8, 114.3, 115.6, 115.8, 124.2, 124.5, 129.4, 130.6, 130.9, 132.1, 133.7, 134.2, 135.2, 143.6, 159.8, 163.1. Anal. Calcd for $C_{21}H_{12}BrClN_4$: C, 57.89; H, 2.78; N, 12.86. Found: C, 57.76; H, 2.90; N, 12.80.

4.4.2. 2-Amino-4-(4-chlorophenyl)-6-(4-methylphenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6b). Pale yellow crystals; mp 229–231 °C. IR (KBr): 3396, 3303, 3206, 2919, 2215, 1642, 1602, 1567, 1552, 1488, 1397, 1327, 1213, 1183, 1097, 1015, 973, 838, 812. ^1H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, CH_3), 6.60 (d, J=15.6 Hz, 1H, CH), 7.20 (d, J=15.6 Hz, 1H, CH), 7.22 (d, J=8.0 Hz, 2H, ArH), 7.39 (d, J=8.4 Hz, 2H, ArH), 7.53 (d, J=8.0 Hz, 2H, ArH), 7.68 (d, J=8.4 Hz, 2H, ArH), 9.24 (s, 1H, NH), 9.40 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.4, 102.7, 114.4, 115.6, 115.9, 122.8, 128.7, 129.3, 129.8, 130.8, 132.2, 133.9, 135.1, 141.0, 145.0, 160.2, 163.3. Anal. Calcd for $C_{22}H_{15}ClN_4$: C, 71.25; H, 4.08; N, 15.11. Found: C, 71.51; H, 4.04; N, 15.00.

4.4.3. 2-Amino-4-(2,4-dichloro-5-fluorophenyl)-6-(4-methoxyphenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6c). Pale yellow crystals; mp 190–192 °C. IR (KBr): 3441, 3308, 3186, 3098, 2220, 1651, 1578, 1477, 1338, 1278, 1244, 1129, 1092, 1033, 893, 820, 733, 669. ^1H NMR (400 MHz, DMSO-d_6): δ 3.79 (s, 3H, CH_3O), 6.62 (d, J=15.6 Hz, 1H, CH), 6.97 (d, J=8.8 Hz, 2H, ArH), 7.03 (d, J=6.0 Hz, 1H, ArH), 7.10 (d, J=15.6 Hz, 1H, CH), 7.66 (d, J=8.4 Hz, 2H, ArH), 8.15 (d, J=6.4 Hz, 1H, ArH), 9.21 (s, 1H, NH), 9.26 (s, 1H, NH). ^{13}C NMR

(100 MHz, DMSO-d_6): δ 52.6, 55.6, 103.1, 114.4, 114.7, 115.1, 115.3, 119.8, 120.1, 122.3, 122.6, 127.6, 128.1, 128.2, 130.9, 132.0, 132.1, 155.2, 157.0, 161.7, 162.4. Anal. Calcd for $C_{22}H_{13}Cl_2FN_4O$: C, 60.15; H, 2.98; N, 12.75. Found: C, 59.97; H, 3.13; N, 12.66.

4.4.4. 2-Amino-4-(2,4-dichloro-5-fluorophenyl)-6-(2-chlorophenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6d). Pale yellow crystals; mp 221–223 °C. IR (KBr): 3415, 3315, 3223, 3065, 2224, 2213, 1637, 1604, 1573, 1549, 1468, 1443, 1391, 1296, 1241, 1094, 1050, 975, 890, 758, 736. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.83 (d, J=16.0 Hz, 1H, CH), 7.35 (d, J=16.0 Hz, 1H, CH), 7.44–7.53 (m, 4H, ArH), 8.02–8.05 (m, 1H, ArH), 8.19 (d, J=6.4 Hz, 1H, ArH), 9.29 (s, 2H, NH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 52.9, 106.5, 113.8, 114.2, 114.8, 122.7, 122.9, 124.9, 128.0, 128.3, 128.9, 130.2, 132.2, 132.3, 133.9, 134.26, 134.33, 155.1, 156.0, 156.1, 161.7, 162.5. Anal. Calcd for $C_{21}H_{10}Cl_3FN_4$: C, 56.85; H, 2.27; N, 12.63. Found: C, 56.99; H, 2.30; N, 12.54.

4.4.5. 2-Amino-4-(2,4-dimethylphenyl)-6-(3,4-dichlorophenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6e). Pale yellow crystals; mp 250–252 °C. IR (KBr): 3372, 3311, 3214, 2923, 2220, 1638, 1613, 1543, 1471, 1384, 1310, 1273, 1209, 1132, 1079, 1028, 968, 825. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.17 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.42 (d, J=15.6 Hz, 1H, CH), 7.08 (s, 1H, ArH), 7.18–7.21 (m, 2H, ArH), 7.35 (d, J=15.6 Hz, 1H, CH), 7.62–7.66 (m, 2H, ArH), 8.00 (s, 1H, ArH), 9.18 (s, 1H, NH), 9.39 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.0, 21.1, 52.5, 105.3, 114.5, 115.5, 115.8, 125.6, 127.0, 128.4, 128.6, 130.4, 131.1, 131.5, 131.7, 132.0, 132.7, 135.5, 135.7, 139.2, 141.1, 160.9, 163.0. Anal. Calcd for $C_{23}H_{16}Cl_2N_4$: C, 65.88; H, 3.85; N, 13.36. Found: C, 66.03; H, 3.64; N, 13.28.

4.4.6. 2-Amino-4-(2,4-dimethylphenyl)-6-(4-chlorophenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6f). Pale yellow crystals; mp 239–241 °C. IR (KBr): 3361, 3310, 3205, 3039, 2957, 2922, 2220, 1642, 1614, 1591, 1543, 1488, 1405, 1322, 1207, 1093, 1078, 1010, 968, 821, 810. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.18 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.43 (d, J=15.6 Hz, 1H, CH), 7.15 (s, 1H, ArH), 7.19–7.22 (m, 2H, ArH), 7.27 (d, J=15.6 Hz, 1H, CH), 7.45 (d, J=8.4 Hz, 2H, ArH), 7.66 (d, J=8.4 Hz, 2H, ArH), 9.20 (s, 1H, NH), 9.39 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.0, 21.1, 52.3, 104.6, 114.4, 115.6, 115.7, 124.2, 127.0, 128.6, 129.2, 130.3, 131.5, 131.7, 133.8, 135.1, 135.5, 139.2, 142.3, 161.0, 163.2. Anal. Calcd for $C_{23}H_{17}ClN_4$: C, 71.78; H, 4.45; N, 14.56. Found: C, 71.70; H, 4.61; N, 14.39.

4.4.7. 2-Amino-4-(4-methylphenyl)-6-(4-chlorophenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6g). Pale yellow crystals; mp 246–248 °C. IR (KBr): 3383, 3304, 3190, 2215, 1644, 1611, 1597, 1540, 1508, 1489, 1406, 1327, 1208, 1183, 1089, 1011, 971, 821. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, CH_3), 6.51 (d, J=15.6 Hz, 1H, CH), 7.16 (d, J=15.6 Hz, 1H, CH), 7.29 (m, J=8.0 Hz, 2H, ArH), 7.39 (d, J=8.4 Hz, 2H, ArH), 7.40 (d, J=8.0 Hz, 2H, ArH), 7.46 (s, 2H, NH_2), 7.04 (d, J=8.4 Hz, 2H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.5, 103.2, 114.4, 115.6, 116.1, 124.9, 129.0, 129.2, 129.7, 130.2, 131.9, 133.9, 135.1, 140.2, 143.0, 161.0, 163.5. Anal. Calcd for $C_{22}H_{15}ClN_4$: C, 71.25; H, 4.08; N, 15.11. Found: C, 71.44; H, 4.00; N, 15.20.

4.4.8. 2-Amino-4-(4-methylphenyl)-6-(3,4-dichlorophenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6h). Pale yellow crystals; mp 250–252 °C. IR (KBr): 3445, 3349, 3238, 2218, 1637, 1559, 1515, 1486, 1465, 1457, 1420, 1382, 1132, 1031, 820. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3), 6.63 (d, J=15.6 Hz, 1H, CH), 7.28 (d, J=8.0 Hz, 2H, ArH), 7.36 (d, J=15.6 Hz, 1H, CH), 7.41 (d, J=8.0 Hz, 2H, ArH), 7.65 (d, J=8.4 Hz, 1H, ArH), 7.69 (d, J=8.4 Hz, 1H, ArH), 8.04 (s, 1H, ArH), 9.18 (s, 1H, NH), 9.34 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.6, 103.8, 114.5, 115.6, 116.1, 126.3, 128.4, 129.1, 129.7, 130.3, 131.2, 131.9, 132.0, 132.7, 135.8, 140.2, 141.8, 160.9, 163.4. Anal. Calcd for $C_{22}H_{14}Cl_2N_4$: C, 65.20; H, 3.48; N, 13.82. Found: C, 65.11; H, 3.44; N, 13.70.

4.4.9. 2-Amino-4-(4-methylphenyl)-6-(2-chlorophenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6i). Pale yellow crystals; mp 212–214 °C (lit.[5] 214–215 °C). IR (KBr): 3414, 3312, 3228, 3063, 3026, 2920, 2218, 2209, 1640, 1614, 1550, 1530, 1508, 1470, 1442, 1326, 1308, 1287, 1265, 1187, 1035, 978, 821, 757. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3), 6.98 (d, J=15.6 Hz, 1H, CH), 7.29–7.33 (m, 3H, ArH+CH), 7.42–7.45 (m, 4H, ArH), 7.49–7.51 (m, 1H, ArH), 7.98–8.00 (m, 1H, ArH), 9.24 (s, 1H, NH), 9.39 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.5, 103.9, 114.4, 115.6, 116.0, 126.9, 128.1, 128.4, 129.0, 129.7, 130.2, 131.8, 132.0, 132.6, 133.8, 139.3, 140.4, 160.8, 163.4. Anal. Calcd for $C_{22}H_{15}ClN_4$: C, 71.25; H, 4.08; N, 15.11. Found: C, 71.19; H, 4.26; N, 15.24.

4.4.10. 2-Amino-4-(4-methylphenyl)-6-(4-chloro-2-nitrophenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6j). Pale yellow crystals; mp 246–247 °C. IR (KBr): 3379, 3322, 3215, 2220, 2211, 1648, 1549, 1518, 1403, 1340, 1265, 969, 839, 829. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3), 6.97 (d, J=15.6 Hz, 1H, CH), 7.30–7.33 (m, 3H, ArH), 7.42 (d, J=8.0 Hz, 2H, ArH), 7.73 (dd, J=8.8 Hz, J'=16.0 Hz, 1H, ArH), 8.02 (d, J=1.0 Hz, 1H, ArH), 8.09 (d, J=8.8 Hz, 1H, ArH), 9.23 (s, 1H, NH), 9.37 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.7, 97.2, 105.1, 114.5, 115.6, 115.8, 127.0, 128.7, 129.1, 129.6, 130.5, 131.6, 132.5, 138.7, 138.8, 140.4, 146.6, 160.5, 163.1. Anal. Calcd for $C_{22}H_{14}ClN_5O_2$: C, 63.54; H, 3.39; N, 16.84. Found: C, 63.67; H, 3.55; N, 16.78.

4.4.11. 2-Amino-4-(4-methylphenyl)-6-(4-methoxyphenyl)cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6k). Pale yellow crystals; mp 220–221 °C. IR (KBr): 3384, 3303, 3198, 2213, 1643, 1597, 1556, 1508, 1464, 1328, 1305, 1281, 1254, 1171, 1031, 975, 829. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3), 3.79 (s, 3H, CH_3O), 6.59 (d, J=15.6 Hz, 1H, CH), 6.97 (d, J=8.4 Hz, 2H, ArH), 7.10 (d, J=15.6 Hz, 1H, CH), 7.27 (d, J=8.0 Hz, 2H, ArH), 7.40 (d, J=8.0 Hz, 2H, ArH), 7.59 (d, J=8.4 Hz, 2H, ArH), 9.19 (s, 1H, NH), 9.36 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.2, 55.6, 101.3, 114.5, 114.8, 115.7, 116.4, 121.7, 127.7, 129.0, 129.6, 130.4, 132.3, 140.0, 144.4, 161.4, 161.5, 164.0. Anal. Calcd for

$C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.24; H, 5.03; N, 15.22.

4.4.12. 2-Amino-4-(4-methylphenyl)-6-(3-chlorophenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6l). Pale yellow crystals; mp 231–233 °C. IR (KBr): 3430, 3332, 3220, 3066, 2917, 2220, 2208, 1620, 1555, 1538, 1508, 1432, 1327, 1207, 1186, 1096, 970, 824, 787. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.42 (s, 3H, CH_3), 6.63 (d, J=15.6 Hz, 1H, CH), 7.28 (d, J=8.0 Hz, 2H, ArH), 7.53 (d, J=16.0 Hz, 1H, CH), 7.40–7.47 (m, 4H, ArH), 7.60 (d, J=7.6 Hz, 1H, ArH), 7.82 (s, 1H, ArH), 9.19 (s, 1H, NH), 9.36 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 52.6, 103.6, 114.5, 115.7, 116.1, 125.8, 127.2, 128.0, 129.1, 129.7, 130.1, 130.9, 131.9, 134.1, 137.2, 140.2, 142.9, 161.0, 163.5. Anal. Calcd for $C_{22}H_{15}ClN_4$: C, 71.25; H, 4.08; N, 15.11. Found: C, 71.39; H, 4.04; N, 15.28.

4.4.13. 2-Amino-4-(4-methylphenyl)-6-(methylphenyl)-cyclohexa-2,4-diene-1,1,3-tricarbonitrile (6m). Pale yellow crystals; mp 228–231 °C. IR (KBr): 3388, 3302, 3191, 3029, 2917, 2214, 1643, 1602, 1568, 1555, 1508, 1414, 1327, 1209, 1182, 1095, 1019, 972, 828, 813, 747. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.60 (d, J=15.6 Hz, 1H, CH), 7.17–7.24 (m, 3H, ArH+CH), 7.27 (d, J=8.0 Hz, 2H, ArH), 7.41 (d, J=8.0 Hz, 2H, ArH), 7.51 (d, J=8.0 Hz, 2H, ArH), 9.21 (s, 1H, NH), 9.38 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.19, 21.24, 52.3, 102.2, 114.4, 115.6, 116.3, 123.1, 128.5, 129.0, 129.7, 129.9, 132.1, 132.3, 140.1, 140.8, 144.6, 161.3, 163.8. Anal. Calcd for $C_{23}H_{18}N_4$: C, 78.83; H, 5.18; N, 15.99. Found: C, 78.90; H, 5.25; N, 15.76.

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Supplementary data

Crystallographic data for the structures of **3m** and **4b** reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with No. CCDC-638240 and CCDC-638241, respectively. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.03.154.

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10. Crystal data for **3m**: $C_{23}H_{17}N_3O_2$; M=367.40, orange block crystals, 0.38×0.30×0.18 mm, triclinic, space group P-1, a=8.971(3) Å, b=10.693(3) Å, c=11.058(4) Å, α=105.558(5)°, β=109.570(6)°, γ=97.644(5)°, V=933.4(5) Å^3, Z=2, D_c=1.307 g cm^{-3}. F(000)=384, μ(Mo Kα)=0.085 mm^{-1}. Intensity data were collected on Rigaku Mercury diffractometer with graphite monochromated Mo Kα radiation (λ=0.71070 Å) using ω scan mode with 3.21°<θ<25.35°; 3403 unique reflections were measured and 2573 reflections with I>2σ(I) were used in the refinement. Structure solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to R=0.0498 and wR=0.1128. Crystal data for **4b**: $C_{24.5}H_{19.5}ClN_{4.5}O$; M=428.40, pale yellow block crystals, 0.22×0.20×0.14 mm, orthorhombic, space group $Pccn$, a=10.0884(14) Å, b=18.574 (3) Å, c=25.167 (4) Å, α=β=γ=90°, V=4715.8 (11) Å^3, Z=8, D_c=1.207 g cm^{-3}. F(000)=1748, μ(Mo Kα)=0.185 mm^{-1}. Intensity data were collected on CCD area detector diffractometer with graphite monochromated Mo Kα radiation (λ=0.71070 Å) using phi and omega scan mode with 1.62°<θ<26.39°; 4829 unique reflections were measured and 2556 reflections with I>2σ(I) were used in the refinement. Structure solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique to R=0.0844 and wR=0.2642.