Synthesis of Phenanthrene Derivatives through the Reaction of an α,α-Dicyanoolefin with α,β-Unsaturated Carbonyl Compounds

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Phenanthrene derivatives were prepared by reacting an α,α-dicyanoolefin with different α,β-unsaturated carbonyl compounds resulting from *Wittig* reaction of ninhydrin and phosphanylidene or condensation of barbituric acid and an aldehyde. The easy procedure, mild and metal-catalyst free, reaction conditions, good yields, and no need for chromatographic purifications are important features of this protocol. The structures of the product of type **3** and **5** were corroborated spectroscopically (IR, ^{1}H- and ^{13}C-NMR, and EI-MS). A plausible mechanism for this type of reaction is proposed (*Scheme 1*).

Introduction. – The interest for phenanthrene derivatives is connected with the presence of their skeleton in a great number of natural products. They have been found to exert a wide spectrum of biological activities, such as anti-HIV [1], anticancer [2], antimycotic [3], antimalarial [4], and antiviral properties [5]. In addition, studies on various substituted phenanthrene derivatives reveal that they exhibit tumor-inhibitory potential [6], cytotoxicity [7], and anti-inflammatory properties [8]. Moreover, phenanthrene derivatives are well known hydrocarbons found in crude oil [9], soil, and sea sediments [10]. As a consequence, many approaches to this structure have been disclosed in the literature. The traditional pathway is the *Haworth* synthesis, which contains a series of steps including *Friedel–Crafts* acylation, followed by a *Clemmensen* reduction or *Wolff–Kishner* reduction, cyclization, reduction, and dehydrogenation [11]. Other reliable strategies to phenanthrenes are intramolecular condensations of disubstituted biphenyls [12], photocyclization of stilbenes [13], Pd-catalyzed cyclization of arynes with alkynes [14], base-catalyzed ring transformation of 4-*sec*-amino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles [15], carbanion-induced ring transformation of 2*H*-pyran-2-ones and 1-naphthalenone [16], and one-pot multicomponent reactions of aldehydes, malononitrile, 1-tetralone, and NH_4OH [17]. Most of these procedures suffer from the limitation of availability of precursors, low yields, harsh reaction conditions, and low functional group tolerance.

The vinylogous addition, a variant of the *Michael* addition reaction [18], is a technical strategy used for the formation of quaternary stereogenic centers [19], spirocarbocycles [20], and polysubstituted benzene derivatives [21]. The high potential of α,α-dicyanoolefins for generation of vinylogous carbanions has led them to readily react with different electrophiles, such as 1,2-diaza-1,3-dienes [22], dialkyl acetylenedicarboxylates [23], aldehydes [24], ketones [25], nitrostyrenes [26], alkylidene malonates [27], and imines [28].

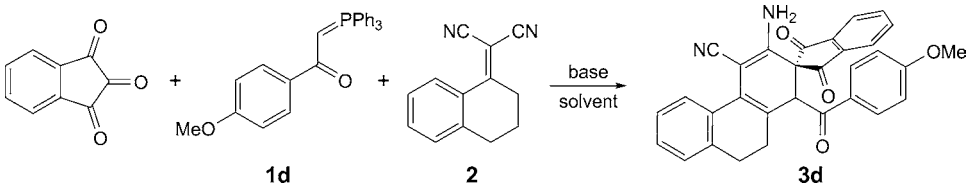
Results and Discussion. – The biological significance of the phenanthrene compounds in mind and in continuation of our researches in the area of multicomponent reaction using vinylogous *Michael* addition methodology [29], herein, we evaluate the one pot reaction of 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)propanedinitrile [30] (**2**), ninhydrin, and phosphanylidene. Our detailed study commenced with refluxing the mixture of ninhydrin and phosphanylidene **1d** in EtOH. Then, the mixture was cooled, and 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)propanedinitrile and Et_3N were added to the mixture at room temperature. Monitoring by TLC revealed that the reactants were consumed to yield a new product **3d**. To establish optimal conditions, several solvents and different bases were explored and the results showed that the reaction proceeded with excellent yields in the presence of Et_3N in EtOH (*Table 1*).

With the optimal conditions established, we turned our attention to investigate the scope of this one-pot transformation by variation of the phosphanylidene component (*Table 2*). It is noticeable that, interpretation of ^{1}H-NMR and ^{13}C-NMR spectra indicates that product **3′a** is obtained as the imino tautomeric form, while product **3b**–**3d** are obtained as the amino tautomer.

As part of our ongoing studies on the development of vinylogous addition of α,α-dicyanoolefins, we next found that 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)propanedinitrile **2** can react with the *Knoevenagel* product **4** of an aromatic aldehyde and barbituric acid in the presence of Et_3N, leading to phenanthrene derivatives **5**. Initially, 5-(arylmethylene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones were prepared according to the literature [31]. The best results for the preparation of **5b** were obtained by performing the reaction in EtOH in the presence of Et_3N (*Table 3*).

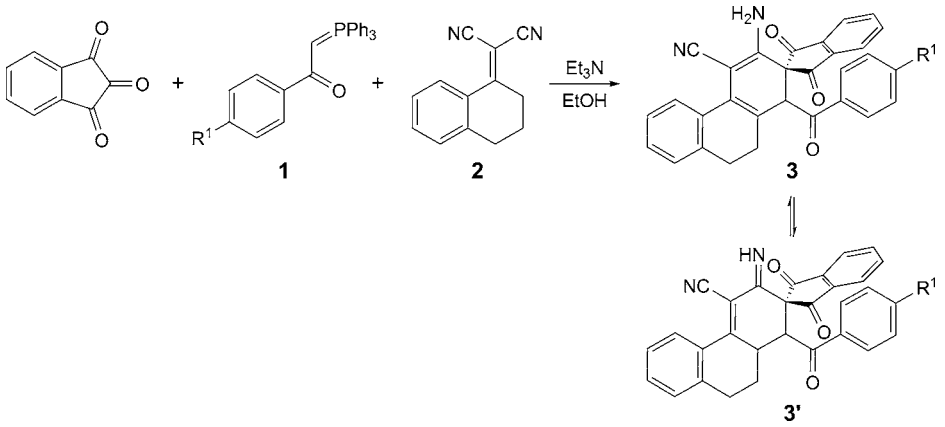
In the next step, we examined the scope of this transformation by variation of the substituent in the aldehyde (*Table 4*). All the products were obtained in good yields.

Table 1. *Results of the Synthesis of* **3d** *under Different Reaction Conditions*



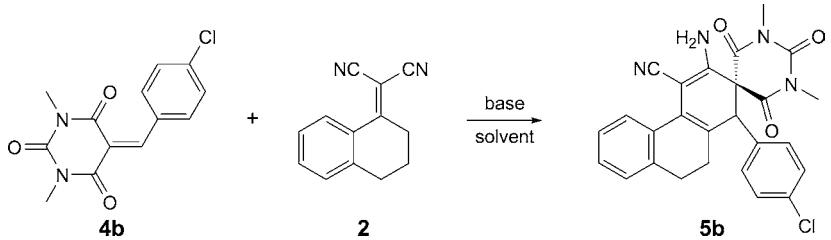
Entry	Solvent	Base	Yield [%]	Time [h]
1	EtOH	Et_3N	78	8
2	EtOH	Na_2CO_3	68	8
3	EtOH	NaOH	65	8
4	MeOH	Et_3N	73	10
5	MeOH	Na_2CO_3	64	10
6	CH_2Cl_2	Et_3N	50	10
7	CH_2Cl_2	Na_2CO_3	45	10
8	MeCN	Et_3N	72	10
9	MeCN	Na_2CO_3	55	10
10	THF	Et_3N	50	12
11	THF	Na_2CO_3	45	12

Table 2. *Synthesis of Phenanthrenes* **3a**–**3d**



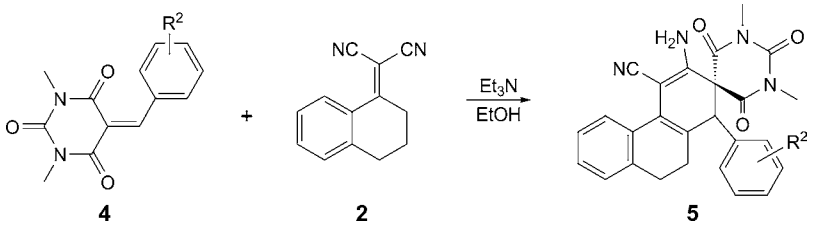
Entry	R^1	Product	Yield [%]
1	H	**3′a**	65
2	Br	**3b**	71
3	Cl	**3c**	74
4	MeO	**3d**	67

Table 3. *Results of the Synthesis of* **5b** *under Different Reaction Conditions*



Entry	Solvent	Base	Yield [%]	Time [h]
1	EtOH	Et_3N	84	1
2	EtOH	Na_2CO_3	72	1
3	EtOH	NaOH	60	1
4	MeOH	Et_3N	78	2
5	MeOH	Na_2CO_3	68	2
6	CH_2Cl_2	Et_3N	60	2
7	CH_2Cl_2	Na_2CO_3	55	2
8	MeCN	Et_3N	76	2
9	MeCN	Na_2CO_3	63	2
10	THF	Et_3N	55	2
11	THF	Na_2CO_3	40	2

Table 4. *Synthesis of Phenanthrenes* **5a**–**5d**



4 **2** **5**

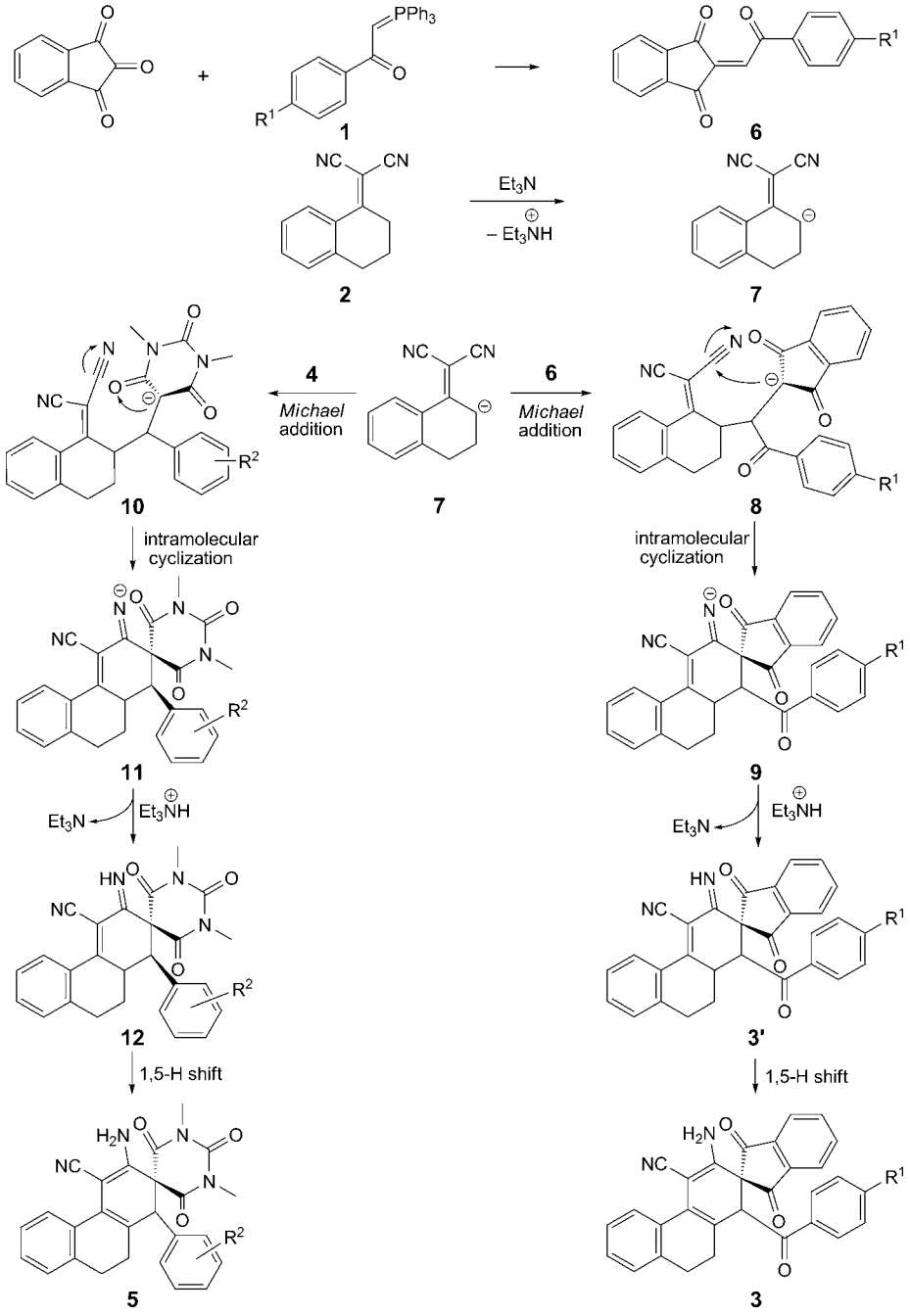
Entry	R^2	Product	Yield [%]
1	3-Br	**5a**	82
2	4-Cl	**5b**	86
3	3-MeO	**5c**	85
4	3-NO_2	**5d**	83

All characterization including mass spectrometric analyses, IR, ^{1}H-NMR, and ^{13}C-NMR proved the structures of the products **3a**–**3d** and **5a**–**5d**. For example, the MS of **3d** displayed the molecular ion peak at *m*/*z* 486, which is in agreement with the proposed structure. In the IR spectrum of **3d**, two absorption bands at 3437 and 3250 cm^{-1}, a sharp band at 2215 cm^{-1}, and absorption bands at 1710, 1659, 1588, and 1109 cm^{-1} attributed to NH_2, CN, C=O, C=C, and C–O stretching frequencies respectively, indicating the most significant functional groups of the product. The ^{1}H-NMR spectrum of **3d** exhibited two *multiplet*s for two CH_2 groups at δ(H) 1.82–1.89 and 2.55–2.67. Three *singlet* signals for MeO, CH, and NH_2 appeared at δ(H) 3.86, 5.67, and 6.92, respectively, and twelve aromatic H-atoms gave rise to characteristic signals in the aromatic region of the spectrum. Observation of 29 distinct signals in the ^{1}H-decoupled ^{13}C-NMR spectrum of **3d** is also in agreement with the proposed structure.

In the IR spectrum of **5c**, absorption bands at 3419 and 3237, at 2216, and at 1750 cm^{-1}, attributed to NH_2, C≡N, and C=O stretching frequencies respectively, indicated the most significant functional groups of the product. The ^{1}H-NMR spectrum of **5a** showed three *multiplet* signals at δ(H) 1.70–1.73, 1.84–1.93, and 2.46–2.55 attributed to two CH_2 groups. Five *singlet* signals at δ(H) 2.91, 2.97, 3.69, 4.48, and 6.98 were ascribed to two MeN and one MeO, CH, and NH_2 groups, respectively. Eight H-atoms of aryl groups appeared in the aromatic region of spectrum. Observation of 26 distinct signals in the ^{1}H-decoupled ^{13}C-NMR spectrum of **5c** is in agreement with the proposed structure.

Based on these results, a plausible mechanism for the formation of the phenanthrene derivatives **3** and **5** has been proposed (*Scheme*). Deportation of α,α-dicyanoolefin **2** with Et_3N furnishes the vinylogous carbanion **7** which attacks the α,β-unsaturated compounds **6** resulting from *Wittig* reaction, or **4**, followed by an intramolecular nucleophilic addition on the CN group (**8** → **9** and **10** → **11**) and protonation (**9** → **3′** and **11** → **12**). By a 1,5-H shift, the imines **3′** and **12** are converted to the corresponding products **3** and **5**.

Scheme. *Mechanistic Rationalization for the Formation of* **3** *and* **5**



To sum up, we have developed a highly convergent one-pot domino protocol for the synthesis of phenanthrene derivatives by using readily available precursors. Other significant advantages of this method include operational simplicity, good yields of products, and that no ligands, acidic medium, metal catalysts, and column chromatography are required.

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Experimental Part

General. M.p.: *Electrothermal 9100*. IR Spectra: *NICOLET FT-IR 100* spectrometer, KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR (300 and 400 MHz) and ^{13}C-NMR (75 and 100 MHz) spectra: *Bruker DRX-400 AVANCE* and *Bruker DRX-500 AVANCE* spectrometers; δ in ppm rel. to Me_4Si as internal standard, J in Hz. MS: *FINNIGAN-MATT 8430* mass spectrometer operating at an ionization potential of 70 eV; in *m*/*z*. Elemental analyses: *Heraeus CHN–O–Rapid* analyzer; in %.

General Procedure 1 (for **3**). A mixture of ninhydrine (1 mmol) and phosphorane **1** (1 mmol) in EtOH (3 ml) was stirred for 30 min at reflux temp. Then, 2-(3,4-dihydronaphthalen-1(2*H*)-ylidene)-propanedinitrile [30] (**2**; 1 mmol) and Et_3N (1 mmol) was added to it, and the mixture was stirred at r.t. After completion, monitored by TLC, the mixture was filtered, and the precipitate was washed with EtOH (2 × 4 ml) to afford the pure product **2**.

General Procedure 2 (for **5**). Et_3N (1 mmol) was added to a soln. of 5-(arylmethylene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-triones **3** (1 mmol) and **2** (1 mmol), and the mixture was stirred at r.t. After completion of the reaction, monitored by TLC, the mixture was filtered, and the precipitate was washed with EtOH (2 × 4 ml) to afford the pure product **5a**–**5d**.

*1′-Benzoyl-1,3,3′,9′,10′,10′a-hexahydro-3′-imino-1,3-dioxo-spiro[2*H*-indene-2,2′(1′*H*)-phenanthrene]-4′-carbonitrile* (**3′a**). Yield: 0.30 g (65%). White powder. M.p. 198–200°. IR: 3226 (NH), 2198 (CN), 1709 (C=O), 1653 (C=O), 1550, 1478 (Ar). ^{1}H-NMR (300.0 MHz, (D_6)DMSO): 1.18–1.85 (*m*, 2 H); 1.87–2.06 (*m*, 2 H); 2.76–2.94 (*m*, 1 H); 3.47–3.40 (*m*, 1 H); 5.08 (*d*, ^3J = 9.5, 1 H); 7.29 (*d*, ^3J = 4.9, 1 H); 7.35–7.44 (*m*, 1 H); 7.46–7.62 (*m*, 3 H); 7.66–7.75 (*m*, 1 H); 7.86–8.13 (*m*, 5 H); 8.18 (*d*, ^3J = 6.7, 1 H); 10.34 (*s*, 1 H). ^{13}C-NMR (100.0 MHz, (D_6)DMSO): 27.5; 29.0; 49.1; 61.7; 71.2; 103.2; 115.8; 123.0; 123.9; 126.3; 128.6; 129.0; 129.3; 129.5; 130.0; 133.0; 134.7; 136.2; 136.5; 136.6; 141.0; 141.6; 142.4; 164.5; 165.2; 195.0; 198.6; 200.7. EI-MS (70 eV): 456 (4, M^+), 438 (2), 413 (44), 394 (13), 351 (89), 333 (47), 306 (13), 292 (9), 267 (41), 252 (13), 239 (18), 226 (8), 203 (9), 190 (13), 165 (9), 152 (8), 133 (9), 105 (100), 91 (8), 77 (95), 51 (8). Anal. calc. for $C_{30}H_{20}N_2O_3$ (456.50): C 78.93, H 4.42, N 6.14; found: C 78.86, H 4.36, N 6.07.

*3′-Amino-1′-(4-bromobenzoyl)-1,3,9′,10′-tetrahydro-1,3-dioxo-1′*H*-spiro[indene-2,2′-phenanthrene]-4′-carbonitrile* (**3b**). Yield: 0.38 g (71%). Green powder. M.p. 217–219° (dec.). IR: 3432, 3249 (NH_2), 2216 (CN), 1708 (C=O), 1671 (C=O), 1588, 1454 (Ar). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.78–1.89 (*m*, 2 H); 2.53–2.67 (*m*, 2 H); 5.64 (*s*, 1 H); 6.97 (*s*, 2 H); 7.18 (*t*, ^3J = 10.0, 1 H); 7.19 (*d*, ^3J = 12.0, 1 H); 7.30 (*t*, ^3J = 7.4, 1 H); 7.41 (*dd*, ^3J = 8.0, 1 H); 7.61 (*d*, ^3J = 7.6, 1 H); 7.75 (*d*, ^3J = 8.0, 1 H); 7.80 (*d*, ^3J = 7.6, 1 H); 7.89 (*d*, ^3J = 7.6, 1 H); 7.96 (*d*, ^3J = 8.0, 1 H); 8.00–8.06 (*m*, 3 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 25.9; 27.8; 53.3; 59.7; 74.9; 120.8; 123.1; 123.7; 124.2; 126.1; 126.8; 126.9; 127.3; 129.0; 130.7; 131.1; 132.2; 132.3; 135.3; 135.6; 136.0; 136.9; 141.9; 141.9; 157.3; 194.8; 197.6; 198.3. EI-MS (70 eV): 534 (1, M^+), 491 (1), 394 (1), 351 (100), 333 (30), 306 (7), 277 (10), 256 (6), 239 (3), 203 (6), 185 (50), 166 (26), 152 (18), 129 (32), 97 (16), 69 (67), 55 (25). Anal. calc. for $C_{30}H_{19}BrN_2O_3$ (535.39): C 67.30, H 3.58, N 5.23; found: C 67.22, H 3.40, N, 5.18.

*3′-Amino-1′-(4-chlorobenzoyl)-1,3,9′,10′-tetrahydro-1,3-dioxo-1′*H*-spiro[indene-2,2′-phenanthrene]-4′-carbonitrile* (**3c**). Yield: 0.37 g (74%). Green powder. M.p. 190–193°. IR: 3438, 3248 (NH_2), 2207 (CN), 1712 (C=O), 1671 (C=O), 1605, 1504 (Ar). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.78–1.87 (*m*, 2 H); 2.51–2.63 (*m*, 2 H); 5.56 (*s*, 1 H); 6.97 (*s*, 2 H); 7.18 (*t*, ^3J = 10.0, 1 H); 7.19 (*t*, ^3J = 11.6, 1 H); 7.30 (*t*, ^3J = 7.2, 1 H); 7.61 (*d*, ^3J = 7.2, 4 H); 7.77 (*d*, ^3J = 7.2, 1 H); 7.88 (*t*, ^3J = 7.6, 1 H); 7.93–8.02 (*m*, 3 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 25.9; 27.8; 53.4; 59.7; 74.9; 120.9; 123.1; 123.7; 124.2; 126.1; 126.8;

127.3; 128.7; 129.4; 130.8; 130.8; 131.9; 135.0; 135.6; 136.0; 136.9; 139.6; 141.9; 141.9; 157.3; 194.8; 197.4; 198.3. EI-MS (70 eV): 491 (9, M^+), 410 (3), 394 (6), 347 (13), 305 (6), 277 (46), 239 (32), 202 (26), 183 (100), 157 (42), 139 (26), 104 (98), 76 (81), 50 (13). Anal. calc. for $C_{30}H_{19}ClN_2O_3$ (490.94): C 73.40, H 3.90, N 5.71; found: C 73.32, H 3.83, N 5.65.

*3′-Amino-1,3,9′,10′-tetrahydro-1′-(4-methoxybenzoyl)-1,3-dioxo-1′*H-*spiro[indene-2,2′-phenanthrene]-4′-carbonitrile* (**3d**). Yield: 0.34 g (68%). Gray powder. M.p. 227–230° (dec.). IR: 3437, 3250 (NH_2), 2215 (CN), 1710 (C=O), 1659 (C=O), 1588, 1403 (Ar), 1109 (C–O). ^{1}H-NMR (400.1 MHz, (D_6)DMSO): 1.82–1.89 (*m*, 2 H); 2.55–2.67 (*m*, 2 H); 3.86 (*s*, 3 H); 5.67 (*s*, 1 H); 6.92 (*s*, 2 H); 7.04 (*d*, ^3J = 8.8, 2 H); 7.20 (*t*, ^3J = 9.6, 2 H); 7.29 (*t*, ^3J = 7.4, 1 H); 7.60 (*d*, ^3J = 7.6, 1 H); 7.85 (*d*, *J* = 7.2, 1 H); 7.93 (*d*, ^3J = 8, 4 H); 7.98–8.04 (*m*, 1 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 25.6; 27.8; 53.6; 55.7; 59.6; 75.00; 114.4; 119.3; 121.6; 122.9; 123.6; 124.1; 126.1; 126.5; 126.7; 127.3; 129.3; 131.4; 131.9; 135.3; 136.0; 136.8; 142.0; 142.1; 157.4; 164.1; 194.8; 196.4; 198.9. EI-MS (70 eV): 486 (1, M^+), 443 (16), 425 (1), 399 (3), 351 (18), 335 (13), 297 (27), 277 (21), 264 (21), 239 (18), 226 (18), 190 (86), 176 (21), 152 (30), 135 (100), 121 (17), 104 (53), 77 (57), 63 (10), 50 (6). Anal. calc. for $C_{31}H_{22}N_2O_4$ (486.52): C 76.53, H 4.56, N 5.76; found: C 76.45, H 4.48, N 5.69.

*3-Amino-1-(3-bromophenyl)-1′,3′,4′,6′,9,10-hexahydro-1′,3′-dimethyl-2′,4′,6′-trioxo-1*H,*2′*H-*spiro[phenanthrene-2,5′-pyrimidine]-4-carbonitrile* (**5a**). Yield: 0.43 g (82%). White powder. M.p. 190–193°. IR: 3417, 3209 (NH_2), 2209 (CN), 1748 (C=O), 1677 (NCON), 1596, 1437 (Ar). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.72–1.87 (*m*, 2 H); 2.42–2.57 (*m*, 2 H); 2.93 (*s*, 3 H); 3.02 (*s*, 3 H); 4.50 (*s*, 1 H); 6.99 (*s*, 2 H); 7.07 (*d*, ^3J = 8.0, 1 H); 7.17–7.31 (*m*, 5 H); 7.52 (*d*, ^3J = 8.0, 1 H); 7.64 (*d*, ^3J = 7.6, 1 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 26.8; 28.2; 28.6; 28.6; 55.1; 61.8; 76.3; 119.4; 121.3; 122.6; 123.7; 125.6; 126.0; 126.9; 127.2; 128.3; 130.4; 131.2; 131.9; 132.1; 136.4; 138.3; 149.9; 155.2; 165.1; 167.5. EI-MS (70 eV): 518 (1, M^+), 498 (1), 437 (1), 362 (12), 334 (4), 321 (64), 307 (4), 281 (37), 266 (29), 243 (26), 226 (4), 209 (21), 194 (91), 180 (24), 166 (40), 152 (23), 129 (100), 116 (35), 101 (52), 75 (40), 56 (35). Anal. calc. for $C_{26}H_{21}BrN_4O_3$ (517.38): C 60.36, H 4.09, N 10.83; found: C 60.27, H 3.99, N 10.79.

*3-Amino-1-(4-chlorophenyl)-1′,3′,4′,6′,9,10-hexahydro-1′,3′-dimethyl-2′,4′,6′-trioxo-1*H,*2′*H-*spiro[phenanthrene-2,5′-pyrimidine]-4-carbonitrile* (**5b**). Yield: 0.41 g (86%). White powder. M.p. 204–205°. IR: 3425, 3252 (NH_2), 2212 (CN), 1751 (C=O), 1680 (NCON), 1598, 1441 (Ar). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.72–1.83 (*m*, 2 H); 2.43–2.54 (*m*, 2 H); 2.91 (*s*, 3 H); 3.02 (*s*, 3 H); 4.47 (*s*, 1 H); 6.95 (*s*, 2 H); 7.07 (*d*, ^3J = 8.4, 1 H); 7.16–7.21 (*m*, 2 H); 7.29 (*td*, ^3J = 7.6, ^2J = 2.0, 1 H); 7.37 (*d*, ^3J = 8.4, 2 H); 7.63 (*d*, ^3J = 7.6, 1 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 26.8; 28.2; 28.6; 55.0; 61.7; 76.4; 119.4; 123.0; 124.0; 125.4; 126.0; 126.8; 127.2; 128.2; 131.12; 132.2; 132.9; 134.7; 136.4; 149.9; 155.2; 165.1; 167.5. EI-MS (70 eV): 472 (3, M^+), 455 (1), 361 (9), 316 (5), 290 (4), 277 (54), 254 (8), 220 (20), 205 (8), 183 (85), 165 (90), 152 (36), 129 (100), 115 (32), 101 (32), 75 (22), 58 (20). Anal. calc. for $C_{26}H_{21}ClN_4O_3$ (472.93): C 66.03, H 4.48, N 11.85; found: C 65.92, H 4.39, N 11.78.

*3-Amino-1′,3′,4′,6′,9,10-hexahydro-1-(3-methoxyphenyl)-1′,3′-dimethyl-2′,4′,6′-trioxo-1*H,*2′*H-*spiro[phenanthrene-2,5′-pyrimidine]-4-carbonitrile* (**5c**). Yield: 0.39 g (85%). White powder. M.p. 234–237°. IR: 3419, 3237 (NH_2), 2216 (CN), 1750 (C=O), 1683 (NCON), 1591, 1443 (Ar). ^{13}H-NMR (400 MHz, (D_6)DMSO): 1.70–1.73 (*m*, 2 H); 1.84–1.93 (*m*, 2 H); 2.46–2.55 (*m*, 2 H); 2.91 (*s*, 3 H); 2.97 (*s*, 3 H); 3.69 (*s*, 3 H); 4.48 (*s*, 1 H); 6.54 (*s*, 1 H); 6.57 (*d*, ^3J = 8.0, 1 H); 6.88 (*d*, ^3J = 7.6, 1 H); 6.98 (*s*, 2 H); 7.18–7.23 (*m*, 3 H); 7.29 (*t*, ^3J = 7.6, 1 H); 7.62 (*d*, ^3J = 7.6, 1 H, CH of Ar). ^{13}C-NMR (100 MHz, (D_6)DMSO): 26.9; 28.2; 28.5; 28.7; 55.0; 56.5; 61.9; 76.4; 113.8; 114.7; 119.5; 121.5; 123.0; 123.8; 125.4; 125.9; 126.7; 127.1; 129.3; 132.3; 136.5; 136.6; 149.8; 155.6; 159.0; 165.1; 168.2. EI-MS (70 eV): 468 (11, M^+), 451 (8), 424 (1), 410 (1), 392 (1), 361 (14), 337 (4), 312 (12), 286 (35), 273 (81), 259 (12), 243 (21), 216 (44), 194 (72), 183 (45), 166 (42), 152 (24), 129 (100), 116 (36), 102 (38), 89 (38), 63 (26), 51 (14). Anal. calc. for $C_{27}H_{24}N_4O_4$ (468.51): C 69.22, H 5.16, N 11.96; found: C 69.13, H 5.06, N 11.86.

*3-Amino-1′,3′,4′,6′,9,10-hexahydro-1′,3′-dimethyl-1-(3-nitrophenyl)-2′,4′,6′-trioxo-1*H,*2′*H-*spiro[phenanthrene-2,5′-pyrimidine]-4-carbonitrile* (**5d**). Yield: 0.48 g (83%). White powder. M.p. 249–251°. IR: 3419, 3267 (NH_2), 2210 (CN), 1747 (C=O), 1682 (NCON), 1597, 1436 (Ar). ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.78–1.87 (*m*, 2 H); 2.37–2.56 (*m*, 2 H); 2.90 (*s*, 3 H); 3.08 (*s*, 3 H); 4.66 (*s*, 1 H); 6.70 (*s*, 2 H); 7.18 (*t*, ^3J = 5.6, 1 H); 7.22 (*d*, ^3J = 7.6, 1 H); 7.31 (*t*, ^3J = 8.8, 1 H); 7.61–7.65 (*m*, 2 H); 7.68 (*d*, ^3J = 7.6, 1 H); 8.03 (*s*, 1 H); 8.18 (*d*, ^3J = 6.4, 1 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 26.8; 28.3; 28.6; 28.8; 53.5; 61.5; 76.2; 119.4; 122.9; 123.3; 123.9; 123.9; 125.6; 126.0; 127.0; 127.3; 129.9; 131.9; 136.0; 136.4;

138.8; 147.4; 150.1; 155.0; 165.3; 166.7. EI-MS (70 eV): 483 (1, M^+), 466 (6), 448 (3), 419 (2), 381 (1), 352 (4), 327 (8), 310 (5), 288 (75), 272 (66), 242 (66), 215 (21), 194 (89), 179 (25), 166 (41), 147 (25), 129 (100), 116 (37), 101 (47), 75 (44), 56 (39). Anal. calc. for $C_{26}H_{21}N_5O_5$ (483.48): C 64.59, H 4.38, N 14.49; found: C 64.30, H 4.29, N 14.39.

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