One-Step Method for the Synthesis of Nitroisoindoles via 1,3-Dipolar Cycloaddition of Azomethine Ylides to Polynitrobenzenes

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Abstract: A new one-step method for the synthesis of nitroisoindoles was developed on the basis of 1,3-dipolar cycloadditions of unstabilized *N*-alkyl azomethine ylides with di- and trinitrobenzenes.

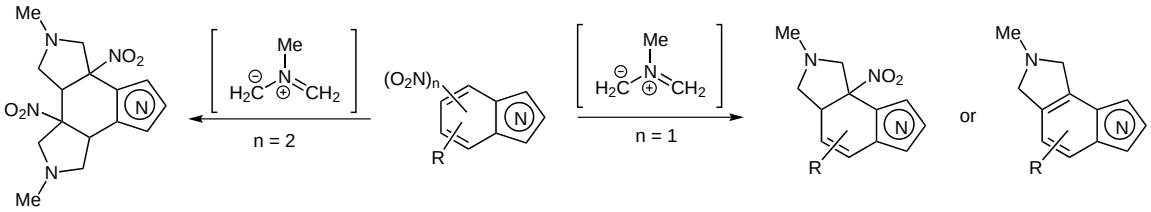
Key words: isoindoles, 1,3-dipolar cycloaddition, nitroarenes, azomethine ylides, heterocycles

Benzo[*c*]pyrroles (isoindoles) and their hydrogenated derivatives are of considerable interest to the researchers since they were found to be useful precursors for a wide range of heterocyclic systems. Many representatives of these heterocycles possess varied biological activity: antihypertonic,[1a] sedative, or CNS stimulating;[1b,1c] some of them were synthesized as potential agents for the symptomatic treatment of benign prostatic hyperplasia (BPH).[1d] Among the known methods for the preparation of compounds of these classes the following are to be mentioned: Wittig's method,[2] synthesis via hydrazine salts,[3] from phthalimidines,[4] and *ortho*-diacylbenzenes.[5] Also of interest are methods for the synthesis of isoindoles by means of annulation of the pyrrole or benzene ring with formation of two C–C bonds, such as interaction of 1,4-diketones with pyrroles[6] or modified Barton–Zard synthesis.[7]

In course of our research on aromatic nitro compounds in cycloaddition reactions we herein report a new simple method for the synthesis of novel functionalized nitroisoindoles on the basis of 1,3-dipolar cycloaddition reactions of *N*-alkyl azomethine ylides with di- and trinitrobenzenes. The first examples of the [3+2] cycloaddition to nitroarenes (aromatic nitro carbocycles) were published recently by our group.[8] These publications dealt with the reactions of nonstabilized *N*-methyl azomethine ylide with mono- and dinitrobenzene fused with azoles and azines (Scheme 1).

In all cases the cycloaddition of one or two double C–C-bond(s) activated by the nitro group was observed giving rise to the loss of aromaticity of the nitrobenzene ring and annulation of the pyrrolidine or pyrroline rings, for example, formation of tetrahydroisoindole or isoindoline systems.[8] Later Lee et al. described[9] a facile dearomatization of nitrobenzene derivatives under the action of *N*-benzyl azomethine ylide giving rise to tetrahydroisoindoles.

In continuation of our recent research we studied the reactions of 1,3,5-trinitrobenzene (TNB, **1**) and its derivatives with symmetrical *N*-methyl azomethine ylide (**2**) that was generated in situ from *N*-methyl glycine and paraformaldehyde on refluxing in toluene (Scheme 2). It was found that instead of the expected annulation of the pyrrolidine ring in contrast to mono- and dinitrobenzazoles[8] (Scheme 1) as well as substituted nitrobenzenes,[9] the reaction of TNB with 1,3-dipole **2** afforded 2-methyl-4,6-dinitroisoindole (**3a**), for example, annulation of a pyrrole ring at only one C–C bond activated by the nitro group. This reaction was accompanied by considerable resinification, therefore the yield of the product was not very high. To the best of our knowledge this is the first example of the one-step isoindole synthesis via 1,3-dipolar cycloaddition of azomethine ylides to nitroarenes. Recently,[8b,10] we found two examples of azomethine ylide utilization for the annulation of pyrrole rings to the benzene cycle of nitroarenes. However, it proceeded in two steps (cycloaddition and oxidation with an external oxidant). In addition, 1,3-dipolar cycloaddition of 1,3-oxazolium-5-olates (münchnones) with benzazoles nitrated at the benzene ring affords the



Scheme 1 1,3-Dipolar cycloaddition of *N*-methyl azomethine ylide with mono- and dinitrobenzazoles

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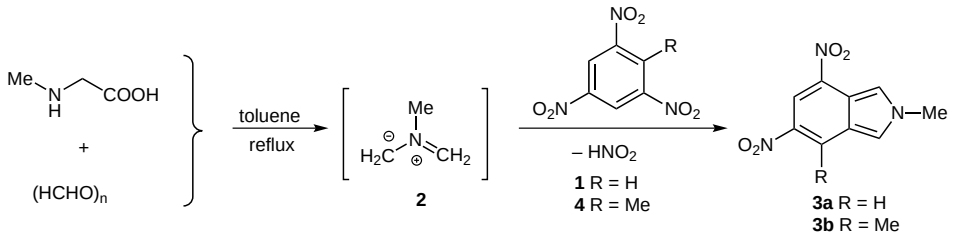


Scheme 2 Reaction of TNB and TNT with *N*-methyl azomethine ylide **2**

pyrrole ring giving rise to the corresponding azoloisoindole derivatives.[11]

Methyl-substituted TNB [2,4,6-trinitrotoluene (TNT, **4**)] under the action of dipole **2** gave the corresponding dimethyl derivative **3b** (Scheme 2). The structures of compounds **3** were assigned using polynuclear 2D NMR experiments. For example, NOE was observed between the protons of the 7-Me group at δ = 2.85 ppm and one of the pyrrole protons in compound **3b** (H-1 at δ = 8.30 ppm). This allowed us to prove unambiguously the direction of the cycloaddition. Moreover, the structure of **3b** was confirmed by single-crystal X-ray crystallographic analysis[12] (Figure 1).

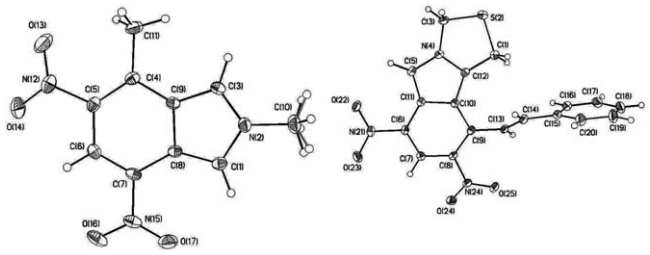
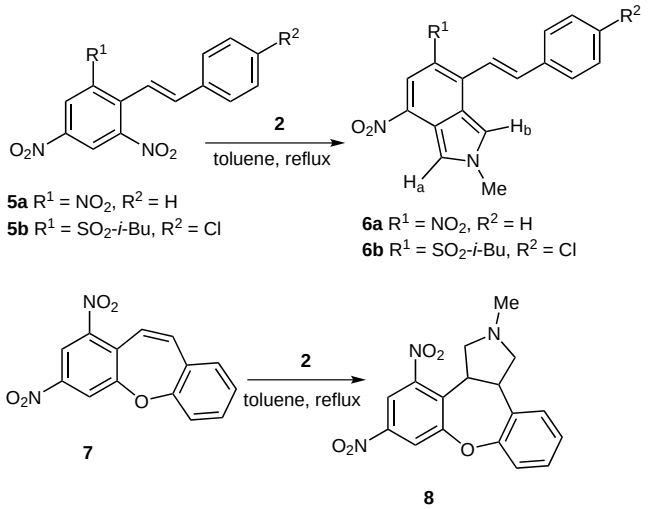


Figure 1 Crystal structure of compounds **3b** (left) and **13b** (right)

Surprisingly, compound **5a** as well as its sulfonyl analogue **5b** (Scheme 3) containing 2-phenylvinyl substituents did not give the corresponding cycloadducts by



Scheme 3 Synthesis of compounds **6a**,**b** and **8** via cycloaddition of *N*-methyl azomethine ylide

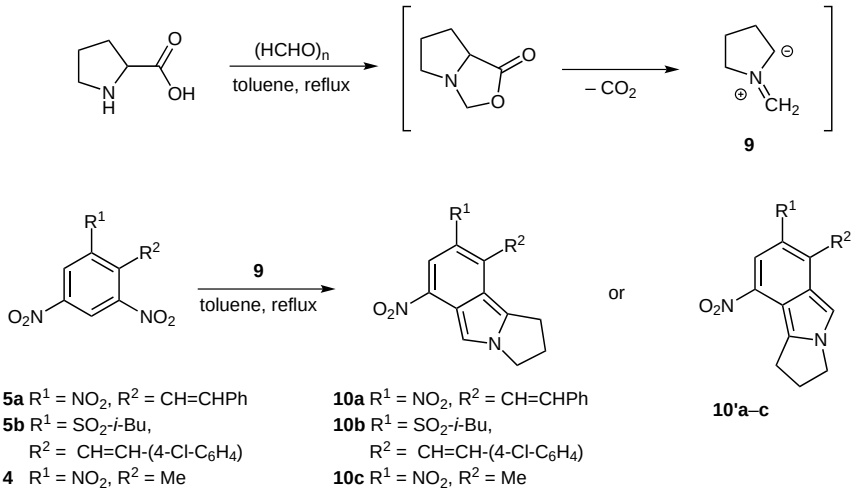
alkenic double bonds. The only products in these cases were isoindoles **6a**,**b**. The ^{1}H NMR spectra of compounds **3** and **6** showed a singlet for the NCH_3 protons at δ = 4.13–4.16 ppm. The protons H_a and H_b of the pyrrole ring usually appeared as two singlets (or sometimes as two doublets with J = 2.0 Hz) in the region of δ = 7.90–8.27 ppm and 8.27–8.60 ppm, respectively. This assignment was made on the basis of 2D NOESY spectra where cross-peaks were observed for H_b and the protons of the double bond. At the same time dinitrobenzoxepin (**7**) under similar conditions afforded tetracyclic adduct **8** (Scheme 3), for example, the cycloaddition to aromatic dinitrobenzene cycle was not favored. It should be noted that in this case only formation of the pyrrolidine derivative occurs as a quite unstable yellow oil whose structure was assigned by ^{1}H NMR spectroscopy.

According to quantum-chemical calculations (performed by D.V. Khakimov, IOC RAS, using HF/STO-3G and B3LYP/6-31G* methods) the plane of the ethylene fragment of **5a** is turned by 42.5° with respect to the plane of the trinitrobenzene ring. Therefore, the conjugation of this double bond with the picryl cycle is quite weak. At the same time in compound **7** the double bond is fixed in the frame of the heterocycle which probably provides the activation of this bond by conjugation with the dinitrobenzene cycle.

Another azomethine ylide **9** can be generated from L-proline and paraformaldehyde (Scheme 4). This cyclic dipole was found to be reactive as well towards polynitro derivatives **5a**,**b** and TNT (**4**), and as a result tricyclic derivatives **10** were isolated.

Although in these cases the formation of two regioisomers **10a**–**c** and **10′a**–**c** is possible, NMR spectroscopic data showed that the structures of the cycloadducts corresponded to **10a**–**c** (Scheme 4). The full assignment of the signals in the NMR spectra was made for compounds **10a**–**c**, and the cross-peaks in the 2D NOESY spectra were observed between the protons of the alkenic double bond (or methyl group for **10c**) and the protons of the cyclic CH_2 groups (Figure 2).

We have found similar regioselectivity in reactions of **4** and **5a** with unsymmetrical dipole **11** which was generated by a standard procedure from L-thiazolidine-4-carboxylic acid and paraformaldehyde (Scheme 5). This reaction afforded isoindolines **12**. In the case of compound **5a** the formation of isoindole **13b** was also observed. Isoindolines **12** were rather stable towards further oxidation



Scheme 4 Reactions of compounds **4** and **5a**,**b** with cyclic azomethine ylide **9**

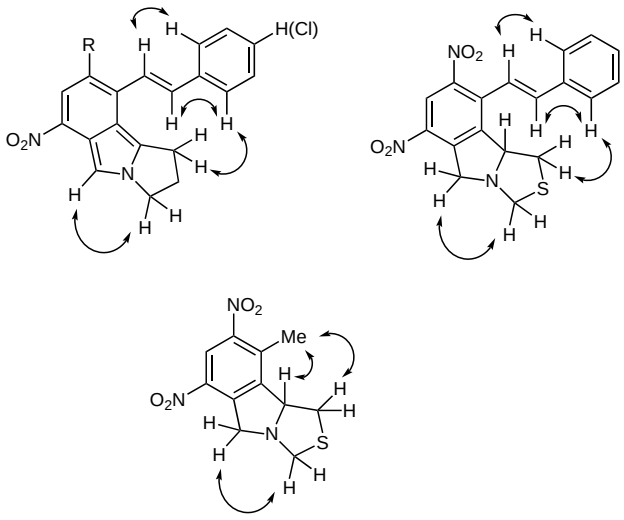


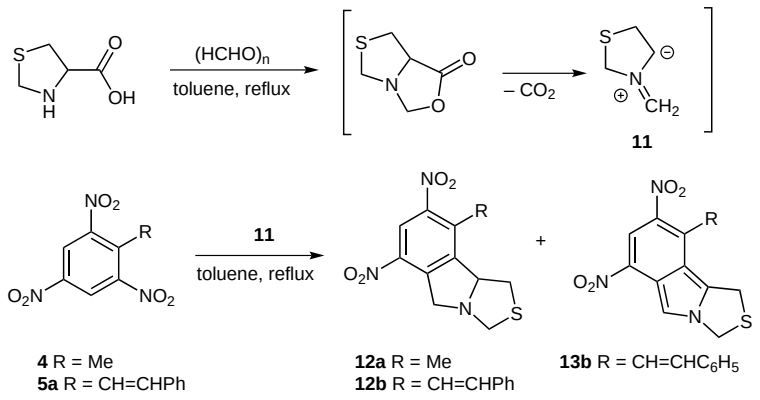
Figure 2 Selected connectivities found in 2D NOESY spectra of the products **10a**,**b** and **12a**,**b**

under the reaction conditions unlike the cycloadducts with other azomethine ylides (see above) where the corresponding intermediate isoindolines could not be isolated due to a rapid oxidation to isoindoles. It should be noted that the ratio of **12b** and **13b** was 1:1 with an overall yield of about 71%. These compounds were separated by flash chromatography and identified separately.

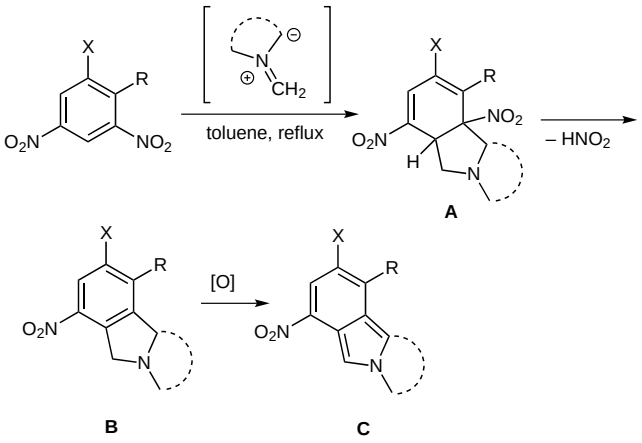
In 2D NOESY spectra of compounds **12** and **13** several interactions were observed proving the structures indicated in Scheme 5 (Figure 2). In addition, the structure of compound **13b** was confirmed by X-ray crystal structure analysis[12] (Figure 1).

In all cases the cycloaddition proceeded regioselectively at the aromatic C–C bond activated by the nitro group in the *ortho* position relative to the R group. The yields of isoindoles were moderate (32–58%) except of those compounds obtained on the basis of TNT (**4**) – the yields of **3b** and **10c** did not exceed 11%. In the case of TNT the side processes are possible due to the deprotonation of the methyl group under the action of bases giving rise to reactive 2,4,6-trinitrobenzyl anions (see, for example, ref.13).

In most cases mentioned above the cycloaddition of azomethine ylide resulted in formation of a pyrrole ring. The only exceptions we found were compounds **12** which could not be completely converted into isoindoles **13** upon prolonged heating. The most probable reaction scheme consists of the cycloaddition itself to give adduct **A**, rearomatization of the benzene ring with loss of nitrous acid and further oxidative dehydrogenation of pyrroline **B**



Scheme 5 Reaction of compounds **4** and **5a** with dipole **11**



Scheme 6 Proposed scheme for the formation of the cycloadducts

either with air oxygen or with starting polynitro compounds present in the reaction mixture (Scheme 6). The latter could explain the moderate yields of the products and the observed resinification of the probable reduction products of polynitro compounds. In addition, when the reactions were carried out under inert atmosphere the product yields were approximately the same.

In conclusion, we developed a new simple one-step method for the annulation of a pyrrole ring to polynitrobenzenes providing a pathway to the previously unknown functionalized nitroisoindoles based on 1,3-dipolar cycloaddition of azomethine ylides to polynitroarenes. The products are not readily available by other methods. All reactions proceed with excellent site selectivity.

Melting points were measured on a Boetius apparatus and are uncorrected. NMR spectra were recorded on a Bruker Avance II 600 spectrometer in DMSO-d_6 or $CDCl_3$ as a solvent. Chemical shifts are reported in ppm downfield from TMS. IR spectra of samples prepared as KBr pellets were recorded on a Bruker Alpha spectrometer. Mass spectra (EI, 70eV) were obtained using a MS-30 Kratos spectrometer. All reactions were monitored by TLC using Silufol plates which were visualized with UV light. Compounds **5a**,**b**[14] and **7**[15] were prepared according to the procedures described in the literature.

Synthesis of the Polycyclic Isoindole Derivatives – General Procedure

A mixture of nitro compound (1 mmol), corresponding amino acid (5 mmol), paraformaldehyde (0.18 g, 6 mmol), and toluene (15 mL) was heated under reflux for 4–6 h (5 min in the case of the synthesis of **6a** and **10a**). After the starting material disappeared (TLC) the mixture was cooled to r.t. and filtered. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on MN Kieselgel 60 (0.04–0.063 mm/230–400 mesh) using $CHCl_3$ to afford the target compounds basically as a red or brown solid.

2-Methyl-4,6-dinitro-2H-isoindole (3a)

Red crystals; mp 236–237 °C; yield 32%. IR (KBr): 3114, 1626, 1566, 1521, 1477, 1331, 1289, 1160, 1063, 799, 725, 623 cm^{-1}. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 4.16 (s, 3 H, CH_3), 7.95 (s, 1 H, H-1), 8.17 (s, 1 H, H-3), 8.60 (s, 1 H, H-7), 9.16 (s, 1 H, H-5). ^{13}C NMR (150.90 MHz, DMSO-d_6): δ = 38.39, 114.22, 114.34, 115.20, 122.97, 124.24, 127.30, 138.10, 138.89. MS: *m/z* = 221 [M^+], 175 [$M^+ – NO_2$], 129 [$M^+ – 2NO_2$]. Anal. Calcd for $C_9H_7N_3O_4$: C, 48.87; H, 3.19; N, 19.00. Found: C, 48.64; H, 3.27; N, 18.82.

2,7-Dimethyl-4,6-dinitro-2H-isoindole (3b)

Red crystals; mp 223–225 °C; yield 11%. IR (KBr): 3167, 3135, 1625, 1567, 1529, 1494, 1347, 1302, 1161, 1014, 787, 620 cm^{-1}. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 2.85 (s, 3 H, 7-CH_3), 4.13 (s, 3 H, 2-CH_3), 7.90 (s, 1 H, H-1), 8.30 (s, 1 H, H-3), 8.54 (s, 1 H, H-5). ^{13}C NMR (150.90 MHz, DMSO-d_6): δ = 17.25, 38.17, 113.50, 115.55, 116.71, 122.13, 126.83, 136.39, 138.61, 139.73. MS: *m/z* = 235 [M^+], 189 [$M^+ – NO_2$], 143 [$M^+ – 2NO_2$]. Anal. Calcd for $C_{10}H_9N_3O_4$: C, 51.07; H, 3.86; N, 17.87. Found: C, 50.76; H, 3.67; N, 17.52.

2-Methyl-5,7-dinitro-4-[(*E*)-2-phenylvinyl]-2H-isoindole (6a)

Dark red crystals; mp 209–211 °C; yield 49%. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 4.14 (s, 3 H, CH_3), 7.39 (d, *J* = 16.2 Hz, 1 H, CH=), 7.41 (t, *J* = 7.2 Hz, 1 H, 4-Ph), 7.47 (t, *J* = 7.4 Hz, 2 H, 3-Ph) 7.73 (d, *J* = 8.4 Hz, 2 H, 2-Ph), 7.80 (d, *J* = 16.3 Hz, 1 H, CH=), 7.98 (d, *J* = 2.0 Hz, 1 H), 8.28 (d, *J* = 1.9 Hz, 1 H), 8.60 (s, 1 H, H-6). ^{13}C NMR (150.90 MHz, DMSO-d_6): δ = 38.71, 114.83, 116.04, 117.36, 123.53, 123.56, 124.48, 127.96, 129.36, 129.69, 136.64, 137.16, 137.88, 137.96, 138.36. MS: *m/z* = 323 [M^+]. Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.16; H, 4.05; N, 13.00. Found: C, 63.21; H, 3.76; N, 12.60.

4-[(*E*)-2-(4-Chlorophenyl)vinyl]-5-(isobutylsulfonyl)-2-methyl-7-nitro-2H-isoindole (6b)

Red crystals; mp 156–158 °C; yield 44%. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 0.92 (d, *J* = 6.7 Hz, 6 H, 2 CH_3), 2.07 (sept, *J* = 6.6 Hz, 1 H, CH), 3.26 (d, *J* = 6.2 Hz, 2 H, CH_2), 4.16 (s, 3 H, NCH_3), 7.49–7.57 (m, 3 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.99 (s, 1 H), 8.05 (d, *J* = 16.4 Hz, 1 H), 8.27 (s, 1 H), 8.47 (s, 1 H). ^{13}C NMR (150.90 MHz, DMSO-d_6): δ = 22.23, 23.85, 38.25, 62.86, 114.88, 115.39, 120.31, 121.17, 123.22, 124.76, 126.83, 129.03, 129.12, 133.85, 135.12, 136.91, 137.14, 140.96. Anal. Calcd for $C_{21}H_{21}ClN_2O_4S$: C, 58.26; H, 4.89; N, 6.47. Found: C, 58.44; H, 4.71; N, 6.59.

2-Methyl-4,6-dinitro-2,3,3a,12b-tetrahydro-1H-dibenzo[2,3:6,7]oxepino[4,5-*c*]pyrrole (8)

Yellow oil; yield 47%. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 2.27 (s, 3 H, CH_3), 2.32–2.46 (m, 2 H), 3.26 (t, *J* = 8.2 Hz, 1 H), 3.36 (t, *J* = 8.2 Hz, 1 H), 3.73 (dd, *J* = 17.9, 10.1 Hz, 1 H), 3.93 (dd, *J* = 18.0, 10.0 Hz, 1 H), 7.14 (t, *J* = 7.3 Hz, 1 H), 7.24–7.29 (m, 2 H), 7.57 (d, *J* = 7.8 Hz, 1 H), 8.51 (d, *J* = 2.1 Hz, 1 H), 8.56 (d, *J* = 2.1 Hz, 1 H).

6,8-Dinitro-9-[(*E*)-2-phenylvinyl]-2,3-dihydro-1H-pyrrolo[2,1-*a*]isoindole (10a)

Dark red crystals; mp 242–243 °C; yield 38%. IR (KBr): 3157, 1557, 1512, 1323, 1287, 1113, 969, 901, 778, 694 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$): δ = 2.68 (t, *J* = 6.9 Hz, 2 H), 3.21 (t, *J* = 6.9 Hz, 2 H), 4.44 (t, *J* = 7.0 Hz, 2 H, NCH_2), 6.82 (d, *J* = 16.3 Hz, 1 H, CH=), 7.42–7.60 (m, 5 H), 7.78–7.86 (m, 2 H), 8.88 (s, 1 H). ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 27.11, 28.16, 48.72, 107.69, 117.63, 118.98, 119.45, 122.70, 127.14, 129.04, 129.16, 135.95, 137.36, 137.67, 139.86, 153.87. MS: *m/z* = 349 [M^+], 257 [$M^+ – 2NO_2$]. Anal. Calcd for $C_{19}H_{15}N_3O_4$: C, 65.32; H, 4.33; N, 12.03. Found: C, 65.17; H, 4.56; N, 12.24.

9-[(*E*)-2-(4-Chlorophenyl)vinyl]-8-(isobutylsulfonyl)-6-nitro-2,3-dihydro-1*H*-pyrrolo[2,1-*a*]isoindole (10b)

Dark red solid; mp 190–192 °C; yield 58%. ^1H NMR (600.13 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 6.8 Hz, 1 H, 2 CH_3), 2.13 (m, 1 H, CH), 2.70 (m, 2 H, CH_2), 3.13 (t, *J* = 7.3 Hz, 2 H, CH_2), 4.43 (t, *J* = 7.3 Hz, 2 H, CH_2), 6.78 (d, *J* = 16.5 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 2 H), 7.55 (d, *J* = 8.3 Hz, 2 H), 7.65 (s, 1 H), 7.96 (d, *J* = 16.5 Hz, 1 H), 8.38 (s, 1 H). ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 22.67, 24.01, 27.05, 27.79, 48.63, 63.67, 107.03, 119.28, 119.76, 120.36, 123.31, 126.26, 128.29, 129.28, 134.27, 135.03, 135.11, 137.13, 137.22,

142.61. Anal. Calcd for $C_{23}H_{23}ClN_2O_4S$: C, 60.19; H, 5.05; N, 6.10. Found: C, 60.34; H, 5.21; N, 5.98.

9-Methyl-6,8-dinitro-2,3-dihydro-1H-pyrrolo[2,1-*a*]isoindole (10c)

Red solid; mp 255–257 °C; yield 11%. IR (KBr): 3158, 1621, 1561, 1525, 1495, 1316, 1286, 1159, 1111, 997, 889, 762, 698 cm^{-1}. ^1H NMR (600.13 MHz, DMSO-d_6): δ = 2.68 (pent, J = 7.3 Hz, 2 H), 2.92 (s, 3 H), 3.47 (t, J = 7.3 Hz, 2 H), 4.44 (t, J = 7.4 Hz, 2 H), 7.87 (s, 1 H), 8.58 (s, 1 H). HRMS: *m/z* calcd for $C_{12}H_{11}N_3O_4$: 262.0822; found: 262.0828. Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.48; H, 4.39; N, 15.78.

9-Methyl-6,8-dinitro-5,9b-dihydro-1H-[1,3]thiazolo[4,3-*a*]isoindole (12a)

Orange solid; mp 133–135 °C; yield 34%. MS: *m/z* = 281 [M^+], 235 [$M^+ - NO_2$], 189 [$M^+ - 2NO_2$]. IR (KBr): 3453, 3117, 1603, 1532, 1352, 1125, 900, 873, 750, 702, 687 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$): δ = 2.65 (s, 3 H, CH_3), 2.83 (dd, J = 11.0, 4.7 Hz, 1 H), 3.44 (dd, J = 11.0, 8.2 Hz, 1 H), 4.35 (s, 2 H), 4.56 (dd, J = 17.8, 1.7 Hz, 1 H), 4.93–4.96 (m, 2 H), 8.73 (s, 1 H). ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 17.12, 39.25, 59.87, 60.86, 72.61, 120.45, 134.07, 140.34, 141.11, 148.20, 149.24. Anal. Calcd for $C_{11}H_{11}N_3O_4S$: C, 46.97; H, 3.94; N, 14.94. Found: C, 47.11; H, 3.99; N, 14.58.

6,8-Dinitro-9-[(*E*)-2-phenylvinyl]-5,9b-dihydro-1H-[1,3]thiazolo[4,3-*a*]isoindole (12b)

Brown solid; mp 160–162 °C; yield 36%. ^1H NMR (600.13 MHz, $CDCl_3$): δ = 2.92 (dd, J = 11.1, 5.1 Hz, 1 H), 3.37 (dd, J = 11.1, 8.1 Hz, 1 H), 4.35 (s, 2 H), 4.57 (d, J = 17.9 Hz, 1 H), 4.96 (d, J = 17.9 Hz, 1 H), 5.12 (t, J = 5.8 Hz, 1 H), 6.94 (d, J = 16.6 Hz, 1 H), 7.27 (d, J = 16.6 Hz, 1 H), 7.39–7.44 (m, 3 H), 7.52 (d, J = 7.2 Hz, 2 H), 8.71 (s, 1 H). ^{13}C NMR (150.90 MHz, $CDCl_3$): δ = 39.59, 59.40, 60.77, 72.94, 119.99, 120.41, 127.16, 129.05, 129.70, 133.83, 135.28, 138.03, 140.73, 146.89, 148.38. Anal. Calcd for $C_{18}H_{15}N_3O_4$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.66; H, 3.91; N, 11.20.

6,8-Dinitro-9-[(*E*)-2-phenylvinyl]-1H-[1,3]thiazolo[4,3-*a*]isoindole (13b)

Dark red crystals; mp 237–239 °C; yield 35%. ^1H NMR (600.13 MHz, $CDCl_3$): δ = 4.35 (s, 2 H), 5.49 (s, 2 H), 6.77 (d, J = 16.3 Hz, 1 H), 7.43–7.62 (m, 5 H), 7.82 (d, J = 16.3 Hz, 1 H), 7.97 (s, 1 H), 8.92 (s, 1 H). ^{13}C NMR (150.90 MHz, DMSO): δ = 30.67, 50.33, 109.22, 117.34, 117.80, 118.07, 122.31, 127.22, 128.92, 129.05, 134.87, 135.74, 136.82, 137.12, 137.50, 139.72. Anal. Calcd for $C_{18}H_{13}N_3O_4S$: C, 58.85; H, 3.57; N, 11.44. Found: C, 58.74; H, 3.72; N, 11.63.

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