SYNTHESIS OF 1*H*-1,2,4-TRIAZOLO[5,1-*a*]ISOINDOLES BY INTRAMOLECULAR CONDENSATION OF 4-SUBSTITUTED 1,2,4-TRIAZOL-1-IUM 4-SUBSTITUTED BENZOYL 2,4,6-TRINITROPHENYLMETHYLIDES

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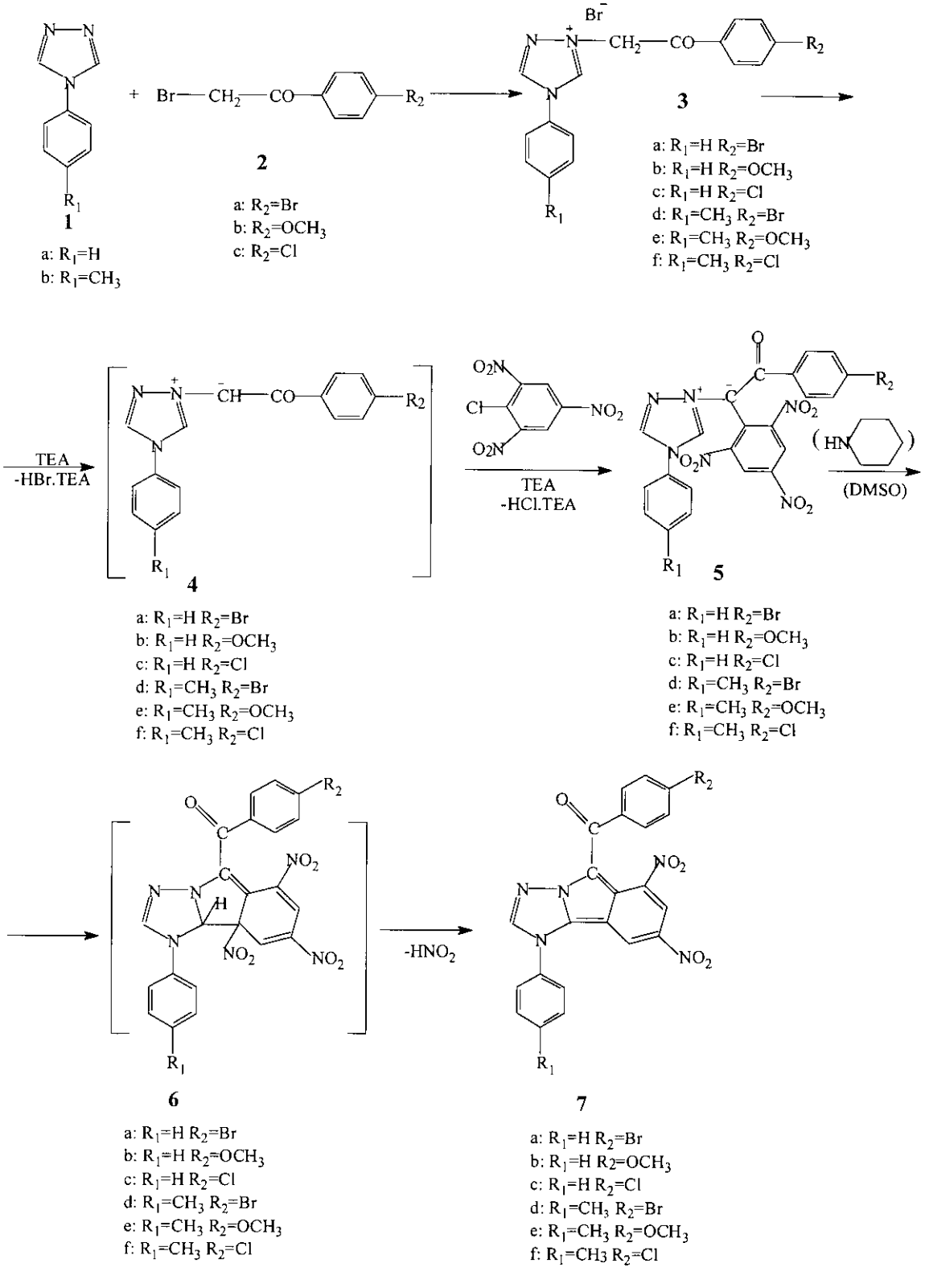
Abstract - The reaction of the 4-substituted 1,2,4-triazol-1-ium 4-substituted benzoyl 2,4,6-trinitrophenylmethylides (**5**) with piperidine gave the 1*H*-1,2,4-triazolo[5,1-*a*]isoindoles (**7**) by a cyclization and then elimination of nitrous acid.

INTRODUCTION

The 1,3,4- and 1,2,4-triazolium ylides are used as reaction intermediates in synthesis of new heterocyclic compounds.[1-3] Usually, the monosubstituted carbanion cycloimmonium ylides react with picryl chloride giving the corresponding disubstituted carbanion cycloimmonium ylides as stable compounds.[4,5] In this paper we used the 1,2,4-triazolium disubstituted carbanion ylides, containing the benzoyl and picryl groups bound to the ylidic carbon atom, in order to obtain new triazolo[5,1-*a*]isoindoles. This procedure represents a new way to the synthesis of isoindole derivatives condensed with an azaheterocyle.

RESULTS AND DISCUSSIONS

The 4-substituted 1,2,4-triazoles (**1**) have been synthesised by a condensation reaction between diformylhydrazine with aniline or *p*-toluidine.[6] The triazoles (**1**) react with 4-substituted 2-bromo-acetophenones (**2**) forming the corresponding triazol-1-ium salts (**3**). This synthesis is known as "the salt method".[7,8]


1
a: R1=H
b: R1=CH3
2
a: R2=Br
b: R2=OCH3
c: R2=Cl
3
a: R1=H R2=Br
b: R1=H R2=OCH3
c: R1=H R2=Cl
d: R1=CH3 R2=Br
e: R1=CH3 R2=OCH3
f: R1=CH3 R2=Cl
TEA
-HBr.TEA
4
a: R1=H R2=Br
b: R1=H R2=OCH3
c: R1=H R2=Cl
d: R1=CH3 R2=Br
e: R1=CH3 R2=OCH3
f: R1=CH3 R2=Cl
TEA
-HCl.TEA
5
a: R1=H R2=Br
b: R1=H R2=OCH3
c: R1=H R2=Cl
d: R1=CH3 R2=Br
e: R1=CH3 R2=OCH3
f: R1=CH3 R2=Cl
(DMSO)
6
a: R1=H R2=Br
b: R1=H R2=OCH3
c: R1=H R2=Cl
d: R1=CH3 R2=Br
e: R1=CH3 R2=OCH3
f: R1=CH3 R2=Cl
-HNO2
7
a: R1=H R2=Br
b: R1=H R2=OCH3
c: R1=H R2=Cl
d: R1=CH3 R2=Br
e: R1=CH3 R2=OCH3
f: R1=CH3 R2=Cl

A mixture of the salt (**3**) and picryl chloride dissolved in chloroform in the presence of triethylamine (TEA) gives the 4-substituted 1,2,4-triazol-1-ium 4-substituted benzoyl 2,4,6-trinitrophenylmethylides (**5**) as stable compounds *via* the reaction of the 4-substituted 1,2,4-triazol-1-ium 4-substituted phenacylides (**4**) with picryl chloride.

By X-Ray diffraction spectra, many spectral arrangements on the level of ylide carbon atoms may be considered.[9] By semiempirical calculations using AM1 and PM3 procedure methods, the values of 14-16 kcal/mol for the rotational barrier around ylide N^+-C^- bond have been obtained.

In order to avoid the decomposition of the ylides generally caused by the cleavage of the N^+-C^- bond, all ylide synthesis has been performed at 0-5°C in the absence of the light.

The reaction of the carbanion ylides (**5**) with piperidine in DMSO at room temperature for 2 hours provided the triazolo[5, 1-*a*]isoindoles (**7**) *via* the cyclic adducts (**6**) followed by a loss of nitrous acid.

All structures of novel compounds have been established by the ^{1}H NMR, IR and MS spectra together with the elemental analytical data.

Generally, the $\nu_{C=O}$ of the ylides appears in the range 1611-1602 cm^{-1}.

All molecular ion peaks of the isoindoles (**7**) have been identified in the MS spectra, and fragment ion peaks corresponding to the triazole ($C_2H_2N_3$) have been observed in all registered spectra.

In the case of all ylides, the fragments produced by the fission of the ylide N^+-C^- bonds are commonly observed.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AM 250 spectrometer, with tetramethylsilane as an internal standard. Chemical shifts are expressed in ppm. MS spectra have been taken on a Platform II Micromass apparatus. IR spectra were recorded on a Perkin Elmer 2000 spectrophotometer. Elemental analytical data have been recorded on a LECO-CHNS 932 apparatus.

General procedure for the synthesis of 1,4-disubstituted-1,2,4-triazol-1-ium bromides

In a 100 mL round-bottomed flask, dissolve 10 mmol of 4-substituted 1,2,4-triazole in 20 mL of acetone. Next, 10 mmol of 4-substituted 2-bromoacetophenones dissolved in 50 mL of acetone are added. The reaction mixture is refluxed on an oil bath for 7 h with magnetic stirring. The formed solid is filtered and then washed with anhydrous ether. A supplementary quantity of salt was obtained by concentration of the filtered solution on a rotary evaporator. The salts were finally purified by recrystallization from ethanol.

1-(4'-Bromophenacyl)-4-phenyl-1,2,4-triazol-1-ium bromide (**3a**). Yield 88%; mp 193°C; IR (KBr), cm^{-1}: 2952, 1697, 1567, 1491, 1460, 1398, 1276, 1097, 1065, 1007, 911, 830, 762; ^{1}H NMR (DMSO-d_6, δ, *J*

Hz): 6.48 (2H, s, NCH_2Ar), 7.62-7.79 (3H, m, H_{arom}), 7.81-7.95 (3H, m, H_{arom}), 7.99-8.10 (3H, m, H_{arom}), 9.95 (1H, s, CH=N), 10.91 (1H, s, $CH=N^+$); MW=423.27: m/z (%): 342.644 (100), 281.161 (1); *Anal.* Calcd for $C_{16}H_{13}N_3OBr_2$, C, 45.40; H, 3.09; N, 9.97. Found C, 45.21; H, 3.12; N, 10.10.

1-(4'-Methoxyphenacyl)-4-phenyl-1,2,4-triazol-1-ium bromide (**3b**). Yield 69%; mp 162-164°C; IR (KBr), cm^{-1} : 3071, 2935, 1672, 1598, 1495, 1353, 1250, 1171, 1097, 995, 825, 764; ^1H NMR (DMSO-d_6, δ, *J* Hz): 3.89 (3H, s, OCH_3), 6.41 (2H, s, NCH_2Ar), 7.16-7.19 (3H, m, H_{arom}), 7.72 (2H, d, *J*=6.2, H_{arom}), 7.93 (2H, d, *J*=6.2, H_{arom}), 8.10 (2H, d, *J*=6.6, H_{arom}), 9.95 (1H, s, CH=N), 10.96 (1H, s, $CH=N^+$); MW=374.42: m/z (%): 294.696 (100), 273.577 (8); *Anal.* Calcd for $C_{17}H_{16}N_3O_2Br$, C, 54.53; H, 4.30; N, 11.27. Found C, 54.35; H, 4.09; N, 11.50.

1-(4'-Chlorophenacyl)-4-phenyl-1,2,4-triazol-1-ium bromide (**3c**). Yield 75%; mp 193-195°C; IR (KBr), cm^{-1} : 3354, 2951, 1587, 1494, 1398, 1345, 1281, 1228, 1091, 1008, 991, 822, 761; ^1H NMR (DMSO-d_6, δ, *J* Hz): 6.45 (2H, s, NCH_2Ar), 7.65-7.70 (5H, m, H_{arom}), 7.90 (2H, d, *J*=8.3, H_{arom}), 8.15 (2H, d, *J*=8.5, H_{arom}), 9.91 (1H, s, CH=N), 10.83 (1H, s, $CH=N^+$); MW=378.84: m/z (%): 298.429 (100), 277.371 (10); *Anal.* Calcd for $C_{16}H_{13}N_3OBrCl$, C, 50.72; H, 3.46; N, 11.14. Found C, 51.01; H, 3.30; N, 11.40.

1-(4'-Bromophenacyl)-4-(4-tolyl)-1,2,4-triazol-1-ium bromide (**3d**). Yield 78%; mp 170°C; IR (KBr), cm^{-1} : 2954, 1693, 1576, 1509, 1397, 1329, 1300, 1225, 1087, 994, 811, 756; ^1H NMR (DMSO-d_6, δ, *J* Hz): 2.43 (3H, s, CH_3), 6.43 (2H, s, NCH_2Ar), 7.53 (2H, d, *J*=8.3, H_{arom}), 7.77 (2H, d, *J*=8.4, H_{arom}), 7.88 (2H, d, *J*=8.6, H_{arom}), 8.04 (2H, d, *J*=8.6, H_{arom}); 9.88 (1H, s, CH=N), 10.78 (1H, s, $CH=N^+$); MW=437.32: m/z (%): 358.540 (100), 281.347 (7); *Anal.* Calcd for $C_{17}H_{15}N_3OBr_2$, C, 46.69; H, 3.45; N, 9.65. Found C, 46.70; H, 3.29; N, 11.04.

1-(4'-Methoxyphenacyl)-4-(4-tolyl)-1,2,4-triazol-1-ium bromide (**3e**). Yield 75%; mp 191°C; IR (KBr), cm^{-1} : 3067, 1693, 1605, 1574, 1518, 1454, 1422, 1358, 1316, 1274, 1177, 1093, 1021, 992, 839, 817, 734; ^1H NMR (DMSO-d_6, δ, *J* Hz): 2.49 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 6.22 (2H, s, NCH_2Ar), 7.05-7.40 (6H, m, H_{arom}), 8.06 (2H, d, *J*=7.7, H_{arom}), 9.30 (1H, s, CH=N), 10.17 (1H, s, $CH=N^+$); MW=388.45: m/z (%): 308.545 (100), 273.520 (1); *Anal.* Calcd for $C_{18}H_{18}N_3O_2Br$, C, 55.65; H, 4.67; N, 10.87. Found C, 55.60; H, 4.58; N, 11.12.

1-(4'-Chlorophenacyl)-4-(4-tolyl)-1,2,4-triazol-1-ium bromide (**3f**). Yield 67%; mp 161-163°C; IR (KBr), cm^{-1} : 3081, 1686, 1577, 1509, 1402, 1229, 1094, 995, 814, 767; ^1H NMR (DMSO-d_6, δ, *J* Hz): 2.43 (3H, s, CH_3), 6.48 (2H, s, NCH_2Ar), 7.58 (2H, d, *J*=8.1, H_{arom}), 7.81 (2H, d, *J*=8.3, H_{arom}), 7.86 (2H, d, *J*=8.2, H_{arom}), 8.22 (2H, d, *J*=8.3, H_{arom}), 9.93 (1H, s, CH=N), 10.93 (1H, s, $CH=N^+$); MW=392.87: m/z (%): 312.517 (100), 277.466 (2); *Anal.* Calcd for $C_{17}H_{15}N_3OBrCl$, C, 51.97; H, 3.84; N, 10.74. Found C, 52.09; H, 3.62; N, 10.94.

General procedure for the synthesis of 4-substituted 1,2,4-triazol-1-ium 4-substituted benzoyl 2,4,6-trinitrophenylmethylides

In a 200 mL two-necked flask equipped with a reflux condenser, a dropping funnel and a magnetically stirrer, dissolve 2.59 mmol of salt (**3**) in 40 mL of dried chloroform. Next, 2.59 mmol of picryl chloride dissolved in 20 mL of dried chloroform are added. The reaction mixture is cooled at 0-5°C in an ice-water bath. By dropping funnel, a solution of 7.7 mmol of triethylamine in 15 mL of dried chloroform is slowly added for 10 min while stirring. The reaction mixture is maintained under argon, without light, for 3 h. The chloroform is removed at a rotary evaporator. A crude triazolium ylide is obtained as a red-violet solid. The pure product has been separated by column chromatography on silica gel using a mixture of petroleum ether-acetone (60:40) as eluent.

4-Bromobenzoyl 4-phenyl-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5a**). Yield 52%; mp 107-109°C; IR (KBr), cm^{-1} : 3090, 1707, 1611, 1541, 1338, 1163, 1068, 1004, 914, 847, 819, 788, 740; ^1H NMR ($CDCl_3$, δ, *J* Hz): 7.01 (2H, d, *J*=8.9, H_{arom}), 7.24 (2H, d, *J*=9.1, H_{arom}), 7.46-7.67 (5H, m, H_{arom}), 8.31 (1H, s, CH=N), 8.72 (2H, s, H_{arom}), 11.09 (1H, s, $CH=N^+$); MW=553.28: m/z (%): 553.062 (36), 508.805 (20), 416.198 (13), 184.482 (43), 145.357 (29); *Anal.* Calcd for $C_{22}H_{13}N_6O_7Br$, C, 47.76; H, 2.36; N, 15.19. Found C, 49.32; H, 2.20; N, 15.70.

4-Methoxybenzoyl 4-phenyl-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5b**). Yield 45%; mp 105°C; IR (KBr), cm^{-1} : 3089, 1707, 1602, 1577, 1538, 1415, 1249, 1160, 1103, 1023, 914, 836, 760, 743; ^1H NMR ($CDCl_3$, δ, *J* Hz): 3.79 (3H, s, OCH_3), 6.72 (2H, d, *J*=8.6, H_{arom}), 7.21 (2H, d, *J*=8.5, H_{arom}), 7.54-7.65 (5H, m, H_{arom}), 8.37 (1H, s, CH=N), 8.70 (2H, s, H_{arom}), 10.94 (1H, s, $CH=N^+$); MW=504.41: m/z (%): 505.703 (100), 145.232 (12), 134.129 (33), 90.318 (12), 75.084 (11); *Anal.* Calcd for $C_{23}H_{16}N_6O_8$, C, 54.76; H, 3.20; N, 16.66. Found C, 54.60; H, 3.20; N, 16.90.

4-Chlorobenzoyl 4-phenyl-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5c**). Yield 54%; mp 111-113°C; IR (KBr), cm^{-1} : 3091, 1609, 1539, 1330, 1164, 1085, 1003, 914, 848, 821, 789, 742; ^1H NMR ($CDCl_3$, δ, *J* Hz): 7.09-7.40 (4H, m, H_{arom}), 7.53-7.59 (5H, m, H_{arom}), 8.28 (1H, s, CH=N), 8.71 (2H, s, H_{arom}), 11.07 (1H, s, $CH=N^+$); MW=508.83: m/z (%): 509.519 (100), 462.128 (15), 369.450 (12), 252.620 (8), 145.161 (27); *Anal.* Calcd for $C_{22}H_{13}N_6O_7Cl$, C, 51.93; H, 2.57; N, 16.51. Found C, 52.04; H, 2.39; N, 16.70.

4-Bromobenzoyl 4-(4-tolyl)-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5d**). Yield 46%; mp 99-101°C; IR (KBr), cm^{-1} : 3089, 2923, 1706, 1607, 1539, 1408, 1304, 1163, 1103, 1067, 1007, 914, 846, 816, 737; ^1H NMR ($CDCl_3$, δ, *J* Hz): 2.48 (3H, s, CH_3), 7.09 (2H, d, *J*=8.5, H_{arom}), 7.31 (2H, d, *J*=8.3, H_{arom}), 7.37-7.48 (4H, m, H_{arom}), 8.33 (1H, s, CH=N), 8.74 (2H, s, H_{arom}), 11.07 (1H, s, $CH=N^+$); MW=567.31: m/z (%): 568.191 (100), 520.413 (30), 474.965 (10), 182.746 (18), 159.360 (84); *Anal.*

Calcd for $C_{23}H_{15}N_6O_7Br$, C, 48.69; H, 2.66; N, 14.81. Found C, 48.49; H, 2.57; N, 14.79.

4-Methoxybenzoyl 4-(4-tolyl)-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5e**). Yield 62%; mp 96-98°C; IR (KBr), cm^{-1} : 3089, 2920, 1707, 1604, 1589, 1249, 1160, 1104, 1024, 914, 816, 763, 742; ^1H NMR ($CDCl_3$, δ, *J* Hz): 2.43 (3H, s, CH_3), 3.75 (3H, s, OCH_3), 6.65 (2H, d; *J*=8.5, H_{arom}), 7.15 (2H, d, *J*=8.5, H_{arom}), 7.29-7.60 (4H, m, H_{arom}), 8.25 (1H, s, CH=N), 8.66 (2H, s, H_{arom}), 10.81 (1H, s, $CH=N^+$); MW=518.44: m/z (%): 519.663 (100), 473.133 (62), 379.417 (12), 159.369 (40), 134.136 (50); *Anal.* Calcd for $C_{24}H_{18}N_6O_8$, C, 55.60; H, 3.50; N, 16.21. Found C, 56.03; H, 3.50; N, 16.50.

4-Chlorobenzoyl 4-(4-tolyl)-1,2,4-triazol-1-ium 2,4,6-trinitrophenylmethylide (**5f**). Yield 61%; mp 103-105°C; IR (KBr), cm^{-1} : 3090, 1609, 1542, 1339, 1164, 1086, 1012, 914, 848, 817, 741, 710; ^1H NMR ($CDCl_3$, δ, *J* Hz): 2.40 (3H, s, CH_3), 7.00-7.10 (4H, m, H_{arom}), 7.24-7.40 (4H, m, H_{arom}), 8.23 (1H, s, CH=N), 8.67 (2H, s, H_{arom}), 10.94 (1H, s, $CH=N^+$); MW=522.86: m/z (%): 523.501 (100), 476.172 (30), 383.987 (12), 159.652 (30), 138.019 (30); *Anal.* Calcd for $C_{23}H_{15}N_6O_7Cl$, C, 52.83; H, 2.89; N, 16.07. Found C, 52.90; H, 2.70; N, 16.59.

General procedure for the synthesis of 1*H*-1,2,4-triazolo[5,1-*a*]isoindoles

In a solution of 0.9 mmol of ylide (**5**) dissolved in 8 mL of DMSO add 0.2 mL of piperidine. The mixture is stirring for 2 h at room temperature, under argon, without light. A net colour change from red-violet to red-orange has been observed. The reaction mixture is treated with 3*N* acetic acid solution until the solid formation. The solid is filtered and washed with water. The crude solid was refluxed in ethanol in an oil bath for 2 h with magnetic stirring. The final pure product is obtained after filtration.

5-(4-Bromobenzoyl)-6,8-dinitro-1-phenyl-1H-1,2,4-triazolo[5,1-a]isoindole (**7a**). Yield 91%; mp 309°C (from ethanol); IR (KBr), cm^{-1} : 3130, 1625, 1587, 1541, 1516, 1445, 1314, 1201, 1067, 856, 830, 761, 737; ^1H NMR ($CDCl_3$, δ, *J* Hz): 7.55-7.80 (9H, m, H_{arom}), 8.37 (1H, s, CH=N), 8.86 (2H, s, H_{arom}); MW=506.27: m/z (%): 506.384 (44), 357.92 (50), 193.920 (43.5), 180.732 (23), 95.473 (25), 59.896 (100); *Anal.* Calcd for $C_{22}H_{12}N_5O_5Br$, C, 52.19; H, 2.39; N, 13.83. Found C, 52.16; H, 2.32; N, 13.89.

5-(4-Methoxybenzoyl)-6,8-dinitro-1-phenyl-1H-1,2,4-triazolo[5,1-a]isoindole (**7b**). Yield 87%; mp 309°C (from ethanol); IR (KBr), cm^{-1} : 3126, 1607, 1538, 1442, 1312, 1265, 1203, 1065, 910, 856, 763; ^1H NMR ($CDCl_3$, δ, *J* Hz): 3.89 (3H, s, OCH_3), 6.96 (2H, d, *J*=9.3, H_{arom}), 7.74-7.78 (5H, m, H_{arom}), 7.86 (2H, d, *J*=9.3, H_{arom}), 8.38 (1H, s, CH=N), 8.87 (2H, s, H_{arom}); MW=457.40: m/z (%): 456.855 (90), 357.93 (45), 255.399 (18), 180.819 (18), 111.827 (20), 87.506 (24), 59.992 (100); *Anal.* Calcd for $C_{23}H_{15}N_5O_6$, C, 60.39; H, 3.30; N, 15.31. Found C, 60.03; H, 3.30; N, 14.93.

5-(4-Chlorobenzoyl)-6,8-dinitro-1-phenyl-1H-1,2,4-triazolo[5,1-a]isoindole (**7c**). Yield 68%; mp 307°C (from ethanol); IR (KBr), cm^{-1} : 3129, 1624, 1541, 1443, 1382, 1312, 1262, 1201, 1095, 1013, 856, 740;

^{1}H NMR ($CDCl_3$, δ, *J* Hz): 7.65-7.89 (9H, m, H_{arom}), 8.36 (1H, s, CH=N), 8.83 (2H, s, H_{arom}); MW=461.82: m/z (%): 460.794 (100), 357.938 (16), 255.407 (11), 146.184 (23), 59.848 (92); *Anal.* Calcd for $C_{22}H_{12}N_5O_5Cl$, C, 57.21; H, 2.62; N, 15.16. Found C, 57.20; H, 2.85; N, 14.62.

5-(4-Bromobenzoyl)-6,8-dinitro-1-(4-tolyl)-1H-1,2,4-triazolo[5,1-a]isoindole (**7d**). Yield 60%; mp 306-307°C (from ethanol); IR (KBr), cm^{-1} : 3129, 1624, 1586, 1537, 1445, 1312, 1201, 1068, 1010, 855, 824, 736; ^{1}H NMR ($CDCl_3$, δ, *J* Hz): 2.56 (3H, s, CH_3), 7.57-7.60 (4H, m, H_{arom}), 7.61 (2H, d, *J*=8.5, H_{arom}), 7.73 (2H, d, *J*=8.5, H_{arom}), 8.31 (1H, s, CH=N), 8.84 (2H, s, H_{arom}); MW=520.29: m/z (%): 520.364 (72), 357.865 (23), 255.539 (18), 180.685 (21), 111.714 (20), 953.41 (23), 59.680 (100); *Anal.* Calcd for $C_{23}H_{14}N_5O_5Br$, C, 53.09; H, 2.71; N, 13.46. Found C, 53.03; H, 3.77; N, 12.96.

5-(4-Methoxybenzoyl)-6,8-dinitro-1-(4-tolyl)-1H-1,2,4-triazolo[5,1-a]isoindole (**7e**). Yield 58%; mp 308°C (from ethanol); IR (KBr), cm^{-1} : 3127, 1597, 1539, 1442, 1381, 1313, 1261, 1203, 1019, 856, 824, 737; ^{1}H NMR ($CDCl_3$, δ, *J* Hz): 2.56 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 6.95 (2H, d, *J*=8.2, H_{arom}), 7.23-7.28 (2H, m, H_{arom}), 7.55-7.62 (2H, m, H_{arom}), 7.85 (2H, d, *J*=8.2, H_{arom}), 8.31 (1H, s, CH=N), 8.84 (2H, s, H_{arom}); MW=471.42: m/z (%): 470.847 (100), 357.813 (18), 255.674 (18), 146.303 (27), 59.880 (70); *Anal.* Calcd for $C_{24}H_{17}N_5O_6$, C, 61.14; H, 3.63; N, 14.85. Found C, 60.31; H, 3.70; N, 14.68.

5-(4-Chlorobenzoyl)-6,8-dinitro-1-(4-tolyl)-1H-1,2,4-triazolo[5,1-a]isoindole (**7f**). Yield 66%; mp 301-302°C (from ethanol); IR (KBr), cm^{-1} : 3129, 1624, 1538, 1445, 1380, 1313, 1202, 1091, 1013, 855, 736; ^{1}H NMR ($CDCl_3$, δ, *J* Hz): 2.56 (3H, s, CH_3), 7.44 (2H, d, *J*=7.9, H_{arom}), 7.52-7.62 (4H, m, H_{arom}), 7.77 (2H, d, *J*=7.9, H_{arom}), 8.31 (1H, s, CH=N), 8.82 (2H, s, H_{arom}); MW=475.84: m/z (%): 474.742 (100), 448.843 (6), 357.797 (2), 59.904 (35); *Anal.* Calcd for $C_{23}H_{14}N_5O_5Cl$, C, 58.05; H, 2.96; N, 14.71. Found C, 58.50; H, 2.67; N, 14.53.

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