

## Supplementary information

### Experimental

#### General

Chemicals were purchased from Sigma-Aldrich and Sisco Research Laboratories and were used without further purification. All reactions and purity of triazole[1,2-*a*]indazole-trione derivatives were monitored by thin-layer chromatography (TLC) using aluminium plates coated with silica gel F<sub>254</sub> plates (Merck) using 30% ethyl acetate and 70% hexane as an eluent. The spots were detected either under ultraviolet (UV) light or by placing in iodine chamber. Melting points were determined in open capillary tubes using a Thomas Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer FTIR-1710 spectrophotometer using nujol film. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECX 400P FT NMR spectrometer using tetramethylsilane (TMS) as an internal standard and the value of chemical shift values were recorded on the δ scale and coupling constants (*J*) values are in hertz (Hz). Mass spectra were Waters LCT micromass spectrometer. Elemental analysis was performed on a Hereaus CHN rapid analyzer. The temperature of the reaction mixture was measured through a non-contact infrared mini gun thermometer (AZ minigun type, model 8868).

#### General procedure for the synthesis of triazole[1,2-*a*]indazole-trione derivatives

A mixture of urazole **1** (1 mmol), aldehyde RCHO **2(a-o)** (1.2 mmol), cyclic β-diketone **3a** (C<sub>6</sub>H<sub>8</sub>O<sub>2</sub>) or **3b** (C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>) (1 mmol) and sulfamic acid (20 mol%) were stirred in water (10 ml) at 50°C until the TLC indicated the completion of the reaction. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate (5 ml × 3) was added to the reaction mixture to extract the product. The combined organic layers were washed with water and dried over anhydrous sodium sulphate and concentrated under reduced pressure to obtain the neat product. Products thus obtained were subjected to purification either by recrystallization from absolute ethanol or column chromatography on silica gel (100-200 mesh size) using hexane/ethyl acetate in varying proportions as eluent which afforded the respective triazole[1,2-*a*]indazole-trione derivatives, **4(a-u)**. All the synthesized products were stable solids and their authenticity was established on the

basis of their spectral analysis (IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and ESI-MS) and elemental analysis data. The spectral data for synthesized compounds are listed below.

### Recycling and reusability of sulfamic acid

One of the unique features of sulfamic acid is its immiscibility with common organic solvents. Thus upon completion of the reaction, the product was extracted using ethyl acetate and dried over anhydrous sodium sulphate and evaporated under reduced pressure to obtain the product. The water extract that was remaining contained sulfamic acid catalyst which was used as such for the consecutive runs without any appreciable loss in its catalytic activity up to four runs

### Spectral data for the synthesized derivatives 4(a-u)

**5,6,7,9-Tetrahydro-9-(phenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4a)** : M.Pt.: 246-250°C; IR (film,  $\nu_{\text{max}}$   $\text{cm}^{-1}$ ) – 3250, 2956, 1782, 1731, 1655;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.93-2.04 (m, 2H,  $\text{CH}_2$ ), 2.25-2.38 (m, 2H,  $\text{CH}_2$ ), 2.47-2.66 (m, 2H,  $\text{CH}_2$ ), 6.08 (s, 1H, CH-Ar), 7.06-7.39 (m, 5H, Ar-H), 10.10 (br s, 1H, NH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  19.6, 27.4, 34.4, 52.7, 116.8, 126.6, 127.4, 127.7, 128.7, 136.4, 139.3, 149.8, 153.6, 192.8; ESI-MS: 282.98 ( $\text{M}^+$ ); Anal calcd. for  $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_3$ : C, 63.60; H, 4.63; N, 14.83; Found : C, 63.28; H, 4.49; N, 14.66.

**5,6,7,9-Tetrahydro-9-(4-chlorophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4b)** : M.Pt.: 182-186°C; IR (film,  $\nu_{\text{max}}$   $\text{cm}^{-1}$ ) – 3199, 2954, 1782, 1738, 1664;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  2.01-2.30 (m, 2H,  $\text{CH}_2$ ), 2.41-2.63 (m, 2H,  $\text{CH}_2$ ), 2.77-2.92 (m, 2H,  $\text{CH}_2$ ), 4.70 (br s, 1H, NH), 6.00 (s, 1H, CH-Ar), 7.30-7.94 (m, 4H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  19.6, 28.3, 34.3, 52.8, 119.6, 126.5, 127.3, 129.4, 137.1, 139.4, 148.8, 150.6, 191.7; ESI-MS: 316.97 ( $\text{M}^+$ ); Anal calcd. for  $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_3$ : C, 56.70; H, 3.81; N, 13.23; Found : C, 56.54; H, 3.65; N, 13.08.

**5,6,7,9-Tetrahydro-9-(4-methoxyphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4c)** : M.Pt.: 176-180°C; IR (film,  $\nu_{\text{max}}$   $\text{cm}^{-1}$ ) – 3299, 2956, 2365, 1858, 1740, 1665;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  1.95-2.07 (m, 2H,  $\text{CH}_2$ ), 2.26-2.41 (m, 2H,  $\text{CH}_2$ ), 2.55-2.68 (m, 2H,  $\text{CH}_2$ ), 3.73 (s, 3H,  $\text{OCH}_3$ ), 4.75 (br s, 1H, NH), 6.03 (s, 1H, CH-Ar), 6.73-7.22 (m, 4H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  20.3, 28.2, 37.7, 52.9, 55.8, 115.6, 118.8, 127.8, 133.6, 140.7, 149.3, 154.6, 157.9,

194.5; ESI-MS: 313.05 ( $M^+$ ); Anal calcd. for  $C_{16}H_{15}N_3O_4$ : C, 61.34; H, 4.83; N, 13.41; Found: C, 61.20; H, 4.68; N, 13.25.

**5,6,7,9-Tetrahydro-9-(4-methylphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-**

**1,3,8(2*H*,5*H*,9*H*)-trione (4d)**: M.Pt.: 220-224°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3303, 2953, 1782, 1735, 1670;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.93-2.02 (m, 2H,  $CH_2$ ), 2.23 (s, 3H,  $CH_3$ ), 2.29-2.42 (m, 2H,  $CH_2$ ), 2.53-2.64 (m, 2H,  $CH_2$ ), 6.28 (s, 1H, CH-Ar), 6.99-7.77 (m, 4H, Ar-H), 9.94 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  20.2, 21.0, 36.9, 37.1, 116.9, 128.6, 128.8, 135.9, 141.4, 143.8, 149.8, 163.8, 196.6; ESI-MS: 297.04 ( $M^+$ ); Anal calcd. for  $C_{16}H_{15}N_3O_3$ : C, 64.64; H, 5.09; N, 14.13; Found: C, 64.50; H, 4.94; N, 13.91.

**5,6,7,9-Tetrahydro-9-(3-hydroxyphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-**

**1,3,8(2*H*,5*H*,9*H*)-trione (4e)**: M.Pt.: 238-240°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3327, 2917, 1768, 1719, 1685;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.89-2.05 (m, 2H,  $CH_2$ ), 2.29-2.41 (m, 2H,  $CH_2$ ), 2.50-2.68 (m, 2H,  $CH_2$ ), 4.75 (br s, 1H, NH), 6.04 (s, 1H, CH-Ar), 7.11-7.42 (m, 4H, Ar-H), 9.91 (br s, 1H, OH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  19.7, 27.6, 38.8, 54.5, 114.8, 116.6, 118.3, 121.2, 127.5, 137.7, 141.8, 148.6, 153.4, 155.7, 193.6; ESI-MS: 299.0 ( $M^+$ ); Anal calcd. for  $C_{15}H_{13}N_3O_4$ : C, 60.20; H, 4.38; N, 14.04; Found: C, 60.00; H, 4.16; N, 13.90.

**5,6,7,9-Tetrahydro-9-(3-nitrophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-**

**1,3,8(2*H*,5*H*,9*H*)-trione (4f)**: M.Pt.: 146-150°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3089, 2933, 1784, 1735, 1654;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.88-1.94 (m, 2H,  $CH_2$ ), 2.25-2.31 (m, 2H,  $CH_2$ ), 2.34-2.38 (m, 2H,  $CH_2$ ), 6.14 (s, 1H, CH-Ar), 7.30-8.19 (m, 4H, Ar-H), 10.10 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  19.5, 26.8, 33.4, 53.8, 117.7, 120.8, 121.3, 128.6, 130.5, 136.7, 138.9, 145.4, 150.8, 154.6, 196.7; ESI-MS: 328.03 ( $M^+$ ); Anal calcd. for  $C_{15}H_{12}N_4O_5$ : C 54.88; H 3.68; N 17.07; Found: C, 54.64; H, 3.53; N, 16.92.

**5,6,7,9-Tetrahydro-9-(4-nitrophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-**

**1,3,8(2*H*,5*H*,9*H*)-trione (4g)**: M.Pt.: 152-156°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3402, 3082, 2924, 1762, 1711, 1605;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.88-2.16 (m, 2H,  $CH_2$ ), 2.27-2.55 (m, 2H,  $CH_2$ ), 2.60-2.94 (m, 2H,  $CH_2$ ), 4.77 (br s, 1H, NH), 6.12 (s, 1H, CH-Ar), 7.55-8.33 (m, 4H, Ar-H);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  20.2, 28.1, 37.6, 55.4, 118.7, 122.8, 127.7, 139.2, 139.8, 144.6, 148.3, 153.7, 195.2; ESI-MS: 328.02

(M<sup>+</sup>); Anal calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>5</sub>: C, 54.88; H, 3.68; N, 17.07; Found : C, 54.65; H, 3.44; N, 16.87.

**5,6,7,9-Tetrahydro-9-(benzo[1,3]-dioxo-5-yl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4h)** : M.Pt.: 262-266°C; IR (film,  $\nu_{\max}$  cm<sup>-1</sup>) – 3401, 2953, 2127, 1788, 1739, 1647; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.60-1.75 (m, 2H, CH<sub>2</sub>), 1.94-2.04 (m, 2H, CH<sub>2</sub>), 2.18-2.38 (m, 2H, CH<sub>2</sub>), 5.58 (s, 1H, CH-Ar), 5.80 (s, 2H, CH<sub>2</sub>-piperonyl), 6.26-6.75 (m, 3H, Ar-H), 8.56 (br s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  19.3, 27.6, 36.8, 53.8, 100.2, 116.5, 118.8, 120.4, 121.3, 137.8, 140.8, 145.6, 149.8, 151.7, 156.5, 194.7; ESI-MS: 327.03 (M<sup>+</sup>); Anal calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>: C, 58.72; H, 4.00; N, 12.84; Found : C, 58.60; H, 3.84; N, 12.71.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(phenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4i)** : M.Pt.: 150-154°C; IR (film,  $\nu_{\max}$  cm<sup>-1</sup>) – 3200, 2958, 1781, 1735, 1596; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.05 (s, 3H, CH<sub>3</sub>), 1.09 (s, 3H, CH<sub>3</sub>), 2.36 (s, 2H, CH<sub>2</sub>), 2.81 (2H, AB system <sup>2</sup>*J*<sub>HH</sub> = 16.9 Hz, CH<sub>2</sub>), 6.41 (s, 1H, CH-Ar), 7.14-7.65 (m, 5H, Ar-H), 10.00 (br s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  28.4, 28.7, 37.8, 39.6, 53.4, 59.7, 118.7, 126.5, 127.9, 136.8, 148.7, 150.6, 154.6, 194.2; ESI-MS: 311.07 (M<sup>+</sup>); Anal calcd. for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>: C, 65.58; H, 5.50; N, 13.50; Found : C, 65.43; H, 5.35; N, 13.37.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(4-bromophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4j)** : M.Pt.: 192-196°C; IR (film,  $\nu_{\max}$  cm<sup>-1</sup>) – 3016, 2962, 1765, 1701, 1648; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  0.94 (s, 6H, 2 × CH<sub>3</sub>), 2.08 (s, 2H, CH<sub>2</sub>), 2.70 (2H, AB system <sup>2</sup>*J*<sub>HH</sub> = 19.1 Hz, CH<sub>2</sub>), 5.93 (s, 1H, CH-Ar), 6.82-7.61 (m, 4H, Ar-H), 9.84 (br s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  27.2, 28.4, 37.4, 38.7, 52.4, 60.7, 120.7, 125.2, 127.6, 128.7, 143.7, 146.1, 152.4, 156.2, 192.7; ESI-MS: 388.97 (M<sup>+</sup>); Anal calcd. for C<sub>17</sub>H<sub>16</sub>BrN<sub>3</sub>O<sub>3</sub>: C, 52.32; H, 4.13; N, 10.77; Found : C, 52.18; H, 3.97; N, 10.62.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(4-methoxyphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4k)** : M.Pt.: 176-180°C; IR (film,  $\nu_{\max}$  cm<sup>-1</sup>) – 3015, 2931, 1895, 1697, 1599; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.05 (s, 6H, 2 × CH<sub>3</sub>), 2.41 (s, 2H, CH<sub>2</sub>), 2.86 (2H, AB system <sup>2</sup>*J*<sub>HH</sub> = 21.2 Hz, CH<sub>2</sub>), 3.72 (s, 3H, OCH<sub>3</sub>), 5.45 (s, 1H, CH-Ar), 6.70-6.96 (m, 4H, Ar-H), 9.83 (br s, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  26.4, 27.3, 36.5, 38.4, 53.5, 58.9, 60.3, 117.7, 119.2, 127.4, 138.1, 141.7,

148.5, 151.6, 155.4, 194.7; ESI-MS: 341.05 ( $M^+$ ); Anal calcd. for  $C_{18}H_{19}N_3O_4$ : C, 63.33; H, 5.61; N, 12.31; Found : C, 63.20; H, 5.48; N, 12.17.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(4-methylphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4l)** : M.Pt.: 170-174°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3019, 2929, 1897, 1666, 1598;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.99 (s, 3H,  $CH_3$ ), 1.12 (s, 3H,  $CH_3$ ), 2.28 (s, 3H,  $CH_3$ ), 2.36 (s, 2H,  $CH_2$ ), 2.96 (2H, AB system  $^2J_{HH} = 19.0$  Hz,  $CH_2$ ), 5.41 (s, 1H, CH-Ar), 6.88-7.22 (m, 4H, Ar-H), 9.84 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  20.6, 27.8, 28.4, 34.8, 36.2, 52.8, 57.3, 118.6, 126.8, 128.2, 135.9, 140.7, 143.2, 147.5, 156.7, 196.7; ESI-MS: 325.10 ( $M^+$ ); Anal calcd. for  $C_{18}H_{19}N_3O_3$ : C, 66.45; H, 5.89; N, 12.91; Found : C, 66.31; H, 5.72; N, 12.76.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(3-hydroxyphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4m)** : M.Pt.: 122-126°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3413, 2961, 1778, 1734, 1654;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.97 (s, 3H,  $CH_3$ ), 1.00 (s, 3H,  $CH_3$ ), 2.29 (s, 2H,  $CH_2$ ), 2.63 (2H, AB system  $^2J_{HH} = 16.2$  Hz,  $CH_2$ ), 5.80 (s, 1H, CH-Ar), 6.78-6.98 (m, 4H, Ar-H), 8.12 (br s, 1H, NH), 9.80 (br s, 1H, OH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  26.5, 27.4, 34.2, 50.7, 54.7, 116.2, 117.3, 120.3, 121.5, 128.6, 139.4, 141.6, 149.7, 152.2, 158.3, 195.8; ESI-MS: 327.06 ( $M^+$ ); Anal calcd. for  $C_{17}H_{17}N_3O_4$ : C, 62.38; H, 5.23; N, 12.84; Found : C, 62.15; H, 5.10; N, 12.67.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(3-nitrophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4n)** : M.Pt.: 134-138°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3210, 2927, 1762, 1668;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.09 (s, 3H,  $CH_3$ ), 1.25 (s, 3H,  $CH_3$ ), 2.42 (s, 2H,  $CH_2$ ), 2.83 (2H, AB system  $^2J_{HH} = 17.6$  Hz,  $CH_2$ ), 5.51 (s, 1H, CH-Ar), 7.37-8.22 (m, 4H, Ar-H), 10.10 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  29.2, 29.7, 36.4, 53.8, 58.4, 120.8, 122.8, 124.7, 129.6, 133.8, 137.4, 142.7, 149.5, 149.8, 159.7, 194.2; ESI-MS: 356.04 ( $M^+$ ); Anal calcd. for  $C_{17}H_{16}N_4O_5$ : C, 57.30; H, 4.53; N, 15.72; Found : C, 57.10; H, 4.36; N, 15.54.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(4-nitrophenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4o)** : M.Pt.: 224-228°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3110, 2960, 1775, 1708, 1654;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.97 (s, 6H,  $2 \times CH_3$ ), 2.18 (s, 2H,  $CH_2$ ), 2.76 (2H, AB system  $^2J_{HH} = 17.6$  Hz,  $CH_2$ ), 6.10 (s, 1H, CH-Ar), 7.53-8.15 (m, 4H, Ar-H), 10.10 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  28.7, 29.3, 35.2, 52.4, 57.4, 118.8, 122.6, 129.3, 139.7, 146.7, 147.4, 150.8, 154.8, 191.6;

ESI-MS: 356.05 ( $M^+$ ); Anal calcd. for  $C_{17}H_{16}N_4O_5$ : C, 57.30; H, 4.53; N, 15.72; Found: C, 57.08; H, 4.37; N, 15.58.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(2-hydroxyphenyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4p)**: M.Pt.: 110-114°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3064, 2958, 1764, 1712, 1643;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  1.00 (s, 3H,  $CH_3$ ), 1.10 (s, 3H,  $CH_3$ ), 2.30 (s, 2H,  $CH_2$ ), 2.51 (2H, AB system  $^2J_{HH} = 17.6$  Hz,  $CH_2$ ), 4.64 (br s, 1H, NH), 6.02 (s, 1H, CH-Ar), 6.89-7.54 (m, 4H, Ar-H), 10.46 (br s, 1H, OH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  27.4, 28.2, 37.9, 51.8, 53.3, 116.7, 117.4, 121.8, 126.4, 126.8, 128.7, 129.2, 138.4, 149.9, 153.6, 192.7; ESI-MS: 327.05 ( $M^+$ ); Anal calcd. for  $C_{17}H_{17}N_3O_4$ : C, 62.38; H, 5.23; N, 12.84; Found: C, 62.21; H, 5.10; N, 12.70.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(2-thienyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4q)**: M.Pt.: 136-140°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3086, 2959, 1786, 1732, 1668;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.95 (s, 6H,  $2 \times CH_3$ ), 2.35 (s, 2H,  $CH_2$ ), 2.92 (2H, AB system  $^2J_{HH} = 16.9$  Hz,  $CH_2$ ), 6.26 (s, 1H, CH-Ar), 6.68-7.11 (m, 3H, Ar-H), 9.81 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  26.5, 27.3, 35.7, 49.2, 54.8, 118.6, 120.2, 126.7, 127.2, 137.4, 140.8, 147.8, 153.6, 193.8; ESI-MS: 316.98 ( $M^+$ ); Anal calcd. for  $C_{15}H_{15}N_3O_3S$ : C, 56.77; H, 4.76; N, 13.24; Found: C, 56.58; H, 4.62; N, 13.06.

**5,6,7,9-Tetrahydro-6,6-dimethyl-9-(propyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4r)**: M.Pt.: 184-186°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3196, 2959, 2734, 1725, 1601;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.86 (t, 3H,  $^*CH_3CH_2$ ), 0.99 (s, 6H,  $2 \times CH_3$ ), 1.29 (m, 2H,  $^*CH_2CH_3$ ), 2.16 (m, 2H,  $CH^*CH_2CH_2$ ), 2.46 (s, 2H,  $CH_2$ ), 2.94 (2H, AB system  $^2J_{HH} = 17.8$  Hz,  $CH_2$ ), 5.28 (m, 1H, CHN), 8.20 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  15.3, 17.8, 26.8, 27.4, 31.2, 36.4, 39.4, 52.7, 121.8, 140.8, 151.7, 156.4, 195.8; ESI-MS: 277.08 ( $M^+$ ); Anal calcd. for  $C_{14}H_{19}N_3O_3$ : C, 60.63; H, 6.91; N, 15.15; Found: C, 60.46; H, 6.73; N, 14.98.

**5,6,7,9-Tetrahydro-9-(ethyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4s)**: M.Pt.: 132-134°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3206, 2962, 2737, 1714, 1667;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.56 (t, 3H,  $^*CH_3CH_2$ ), 1.39-1.45 (m, 2H,  $^*CH_2CH_3$ ), 1.92-2.00 (m, 2H,  $CH_2$ ), 2.23-2.30 (m, 2H,  $CH_2$ ), 2.37-2.48 (m, 2H,  $CH_2$ ), 4.76 (m, 1H, CHN), 6.12 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  11.2, 20.8, 22.3, 33.4,

38.4, 46.7, 11.6, 139.8, 147.2, 152.2, 193.6; ESI-MS: 235.03 ( $M^+$ ); Anal calcd. for  $C_{11}H_{13}N_3O_3$ : C, 56.16; H, 5.57; N, 17.86; Found : C, 56.03; H, 5.42; N, 17.70.

**5,6,7,9-Tetrahydro-9-(isobutyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4t)** : M.Pt.: 120-124°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3276, 3192, 2952, 1734, 1622;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.85 (d, 6H, 2  $\times$   $CH_3$ ), 1.22 (m, 2H, CH- $CH_2$ ), 1.65 (m, 1H, CH( $CH_3$ ) $_2$ ), 1.94-2.02 (m, 2H,  $CH_2$ ), 2.42-2.46 (m, 2H,  $CH_2$ ), 2.48-2.52 (m, 2H,  $CH_2$ ), 4.08 (m, 1H, CHN), 7.78 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  18.6, 22.7, 24.2, 31.8, 40.6, 44.5, 49.3, 119.6, 138.6, 148.6, 152.4, 192.7; ESI-MS: 263.06 ( $M^+$ ); Anal calcd. for  $C_{13}H_{17}N_3O_3$ : C, 59.30; H, 6.51; N, 15.96; Found : C, 59.13; H, 6.36; N, 15.80.

**5,6,7,9-Tetrahydro-9-(hexyl)-[1,2,4]-triazolo[1,2-*a*]indazole-1,3,8(2*H*,5*H*,9*H*)-trione (4u)** : M.Pt.: 166-168°C; IR (film,  $\nu_{\max}$   $cm^{-1}$ ) – 3086, 2959, 1786, 1732, 1668;  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  0.76 (t, 3H,  $^*CH_3CH_2$ ), 1.36 (m, 2H,  $^*CH_2CH_3$ ), 1.68 (m, 2H, CH- $^*CH_2-CH_2$ ), 1.84 (m, 6H, 3  $\times$   $CH_2$ ), 1.92-1.98 (m, 2H,  $CH_2$ ), 2.23-2.30 (m, 2H,  $CH_2$ ), 2.37-2.44 (m, 2H,  $CH_2$ ), 6.38 (m, 1H, CHN), 8.33 (br s, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  14.8, 19.2, 24.7, 25.2, 28.7, 29.6, 31.8, 33.2, 38.4, 49.6, 119.7, 137.8, 146.6, 151.8, 192.7; ESI-MS: 291.10 ( $M^+$ ); Anal calcd. for  $C_{15}H_{21}N_3O_3$ : C, 61.84; H, 7.27; N, 14.42; Found : C, 61.52; H, 7.12; N, 14.28.