



## Journal Name

### ARTICLE

## Electronic Supplementary Information

### High-yield multicomponent synthesis of triazolo[1,2-a]indazole-triones using silica-coated ZnO nanoparticles as heterogeneous catalyst in the presence of ultrasound

Divya Verma<sup>a</sup>, Vikash Sharma<sup>b</sup>, Gunadhor Singh Okram<sup>b\*</sup> and Shubha Jain<sup>a</sup>

<sup>a</sup>Laboratory of Heterocycles and Nanomaterials, School of Studies in Chemistry & Biochemistry, Vikram University, Ujjain, Madhya Pradesh 456010, India.

<sup>b</sup>UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore, Madhya Pradesh 452001, India.

\*Corresponding Authors:

okram@csr.res.in

divya.vrma10@gmail.com

#### Table of Contents

Table S1. Physicochemical properties of synthesized catalysts

Table S2. Dynamic light scattering data (a) Zeta potential ( $\zeta$ ) data (b) Hydrodynamic diameter (HD) data (c) Electrical Conductivity and Mobility data

Table S3. Effect of temperature on TAIT synthesis.

Figure S1. (a) Micrograph, elemental mapping of (b) Si, Zn and O together, (c) Zn (red) only, (d) Si (green) only, (e) O (blue) only and (f) energy dispersive analysis of X-rays (EDAX) of ZnO@SiO<sub>2</sub> NPs. (g) EDAX of SiO<sub>2</sub> NPs.

Figure S2. UV-Vis absorption spectra of triazolo[1,2-a]indazole-triones using dimedone, 4-phenylurazole and 4-chlorobenzaldehyde

Figure S3. UV-Vis absorption spectra of triazolo[1,2-a]indazole-triones using dimedone, 4-phenylurazole and 4-hydroxybenzaldehyde.

Figure S4. XRD patterns of ZnO@SiO<sub>2</sub> NPs after every use as catalyst up to six runs.

Figure S5. Raman spectra of ZnO@SiO<sub>2</sub> nanoparticles after every use as catalyst up to six runs.

Table S4. Spectral data.

Figures S6-S24. Selected FTIR, <sup>13</sup>C NMR, <sup>1</sup>H NMR and MASS of synthesized product.

References

**Table S1. Physicochemical properties of synthesized catalysts**

Catalysts	XRD crystallite size (nm)	TEM crystallite (diameter) size (nm)	d spacing (nm)	Specific surface area (m <sup>2</sup> /g)	Hydrodynamic diameter (nm) (First Run)	Zeta potential (mV) (First Run)
SiO <sub>2</sub>	1.05±0.01	-	-	3.7	30497	-18.89, -13.50, 01.89
ZnO	22.00±0.01	21.5±0.7	0.24	11.7	1073	-13.22
ZnO@SiO <sub>2</sub>	27.64±0.01/ 1.03	48.0±0.1	0.24	97.5	690	-36.53

**Tables S2: Dynamic light scattering (DLS) data**

Tables S2 (a). Hydrodynamic diameter (HD) data of the SiO<sub>2</sub>, ZnO and ZnO@SiO<sub>2</sub> nanoparticles

HD in nm	SiO <sub>2</sub>	ZnO	ZnO@SiO <sub>2</sub>
First run	390, 30497	75, 1073	107, 690
Second run	189, 466, 19202	1202	225, 3081
Third run	178, 915, 28697	1324	752

Tables S2 (b). Zeta potential ( $\zeta$ ) data of the SiO<sub>2</sub>, ZnO and ZnO@SiO<sub>2</sub> nanoparticles

$\zeta$ in mV	SiO <sub>2</sub>	ZnO	ZnO@SiO <sub>2</sub>
First run	-18.89, -13.50, 1.89	-13.22, -4.00	-36.53, -14.26
Second run	-8.44, -0.75	-11.37, -2.94	-34.99, -21.62
Third run	-14.67, -02.37	-10.62, -2.32	-31.70, -17.28

Tables S2 (c). Electrical Conductivity and Mobility data of the SiO<sub>2</sub>, ZnO and ZnO@SiO<sub>2</sub> nanoparticles

Furthermore, to elucidate the catalytic activity of the nanoparticle dispersion, electrical conductivity and mobility of SiO<sub>2</sub>, ZnO and ZnO@SiO<sub>2</sub> NPs are listed in Table S1. ZnO NPs and SiO<sub>2</sub> has lower absolute value of zeta potential, lower mobility and higher conductivity than those of ZnO@SiO<sub>2</sub> where in less agglomeration of particles and hence smaller HD is found.

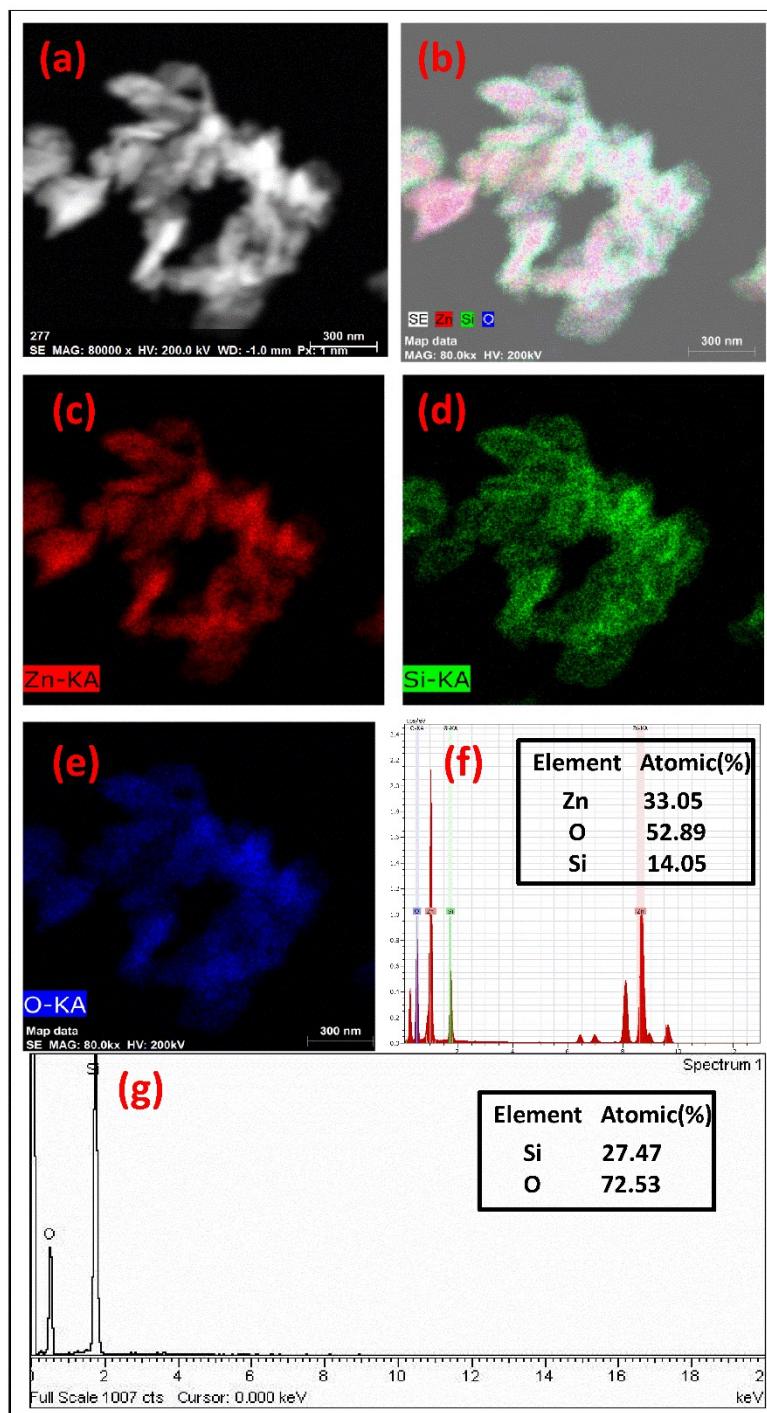
Sample	Run	Zeta Potential (mV)	Mobility cm <sup>2</sup> /Vs	Conductivity mS/cm	Avg. Electric Field (V/cm)
SiO <sub>2</sub>	1	-13.50	$-4.06 \times 10^{-5}$	0.0302	-84.99
	2	-08.44	$-2.89 \times 10^{-5}$	0.0283	-85.00
	3	-02.37	$-2.78 \times 10^{-5}$	0.0279	-84.98
ZnO	1	-13.21	$-1.03 \times 10^{-4}$	0.0258	-84.99
	2	-11.47	$-8.95 \times 10^{-5}$	0.0265	-85.00
	3	-10.84	$-8.45 \times 10^{-5}$	0.0278	-84.98
ZnO@SiO <sub>2</sub>	1	-36.53	$-2.85 \times 10^{-4}$	0.0203	-84.97
	2	-34.99	$-2.69 \times 10^{-4}$	0.0204	-85.00
	3	-31.70	$-2.57 \times 10^{-4}$	0.0196	-85.00

**Table S3. Effect of temperature on TAIT synthesis**

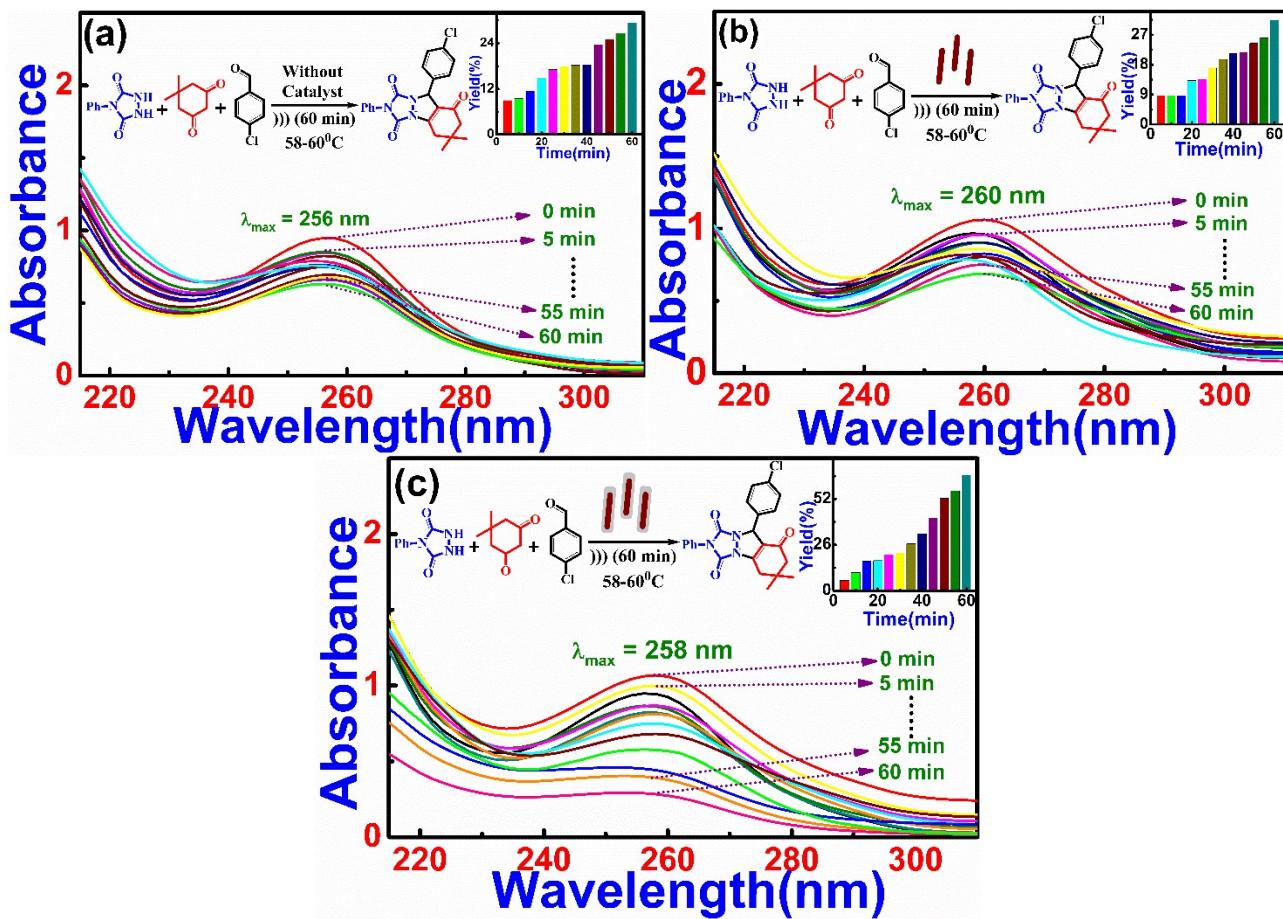
The effect of temperature on the same model reaction to synthesize **4a** has also been investigated. The reaction was carried out by changing the temperatures from room temperature to 70° C. Yields of the product at different temperatures are listed in Table S3. From the Table S3 it is evident that the reaction is more efficient at 60° C and gave 80 % yield.

Entry	Amount of catalyst	Reaction temperature(°C)	Yields(%)	Time(min.)
1.	10 mol %	RT	25	60 min
2.	10 mol %	35	45	60 min
3.	10 mol %	40	60	60 min
4.	10 mol %	50	70	60 min
5.	10 mol %	60	80	60 min
6.	10 mol %	70	82	60 min

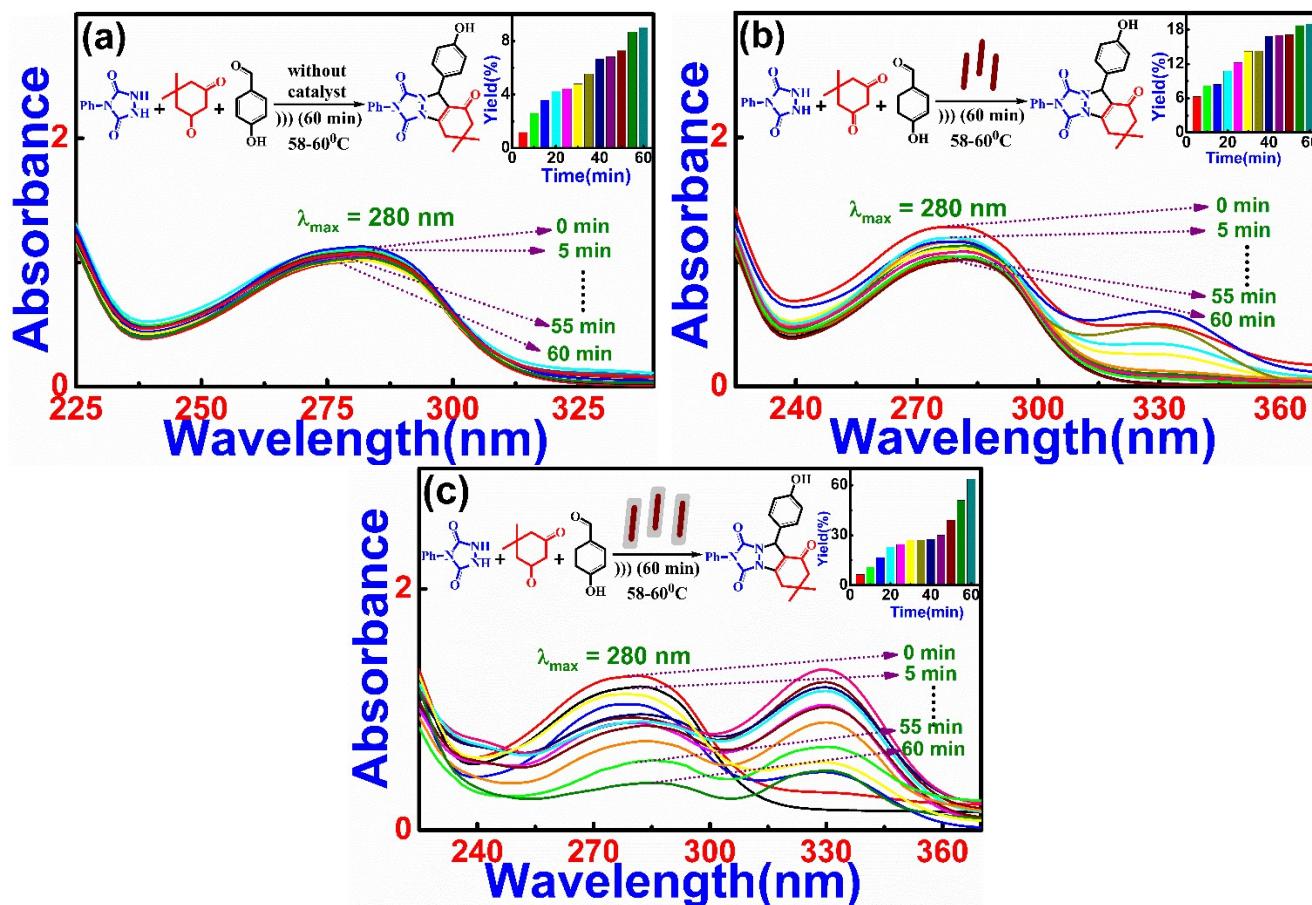
Reaction conditions: 4-phenylurazole **1** (1 mmol), dimedone **2** (1 mmol), benzaldehyde **3** (1 mmol) and ZnO@SiO<sub>2</sub> NPs (10 mol %) in water (10 mL), sonicated at 58–60 °C.



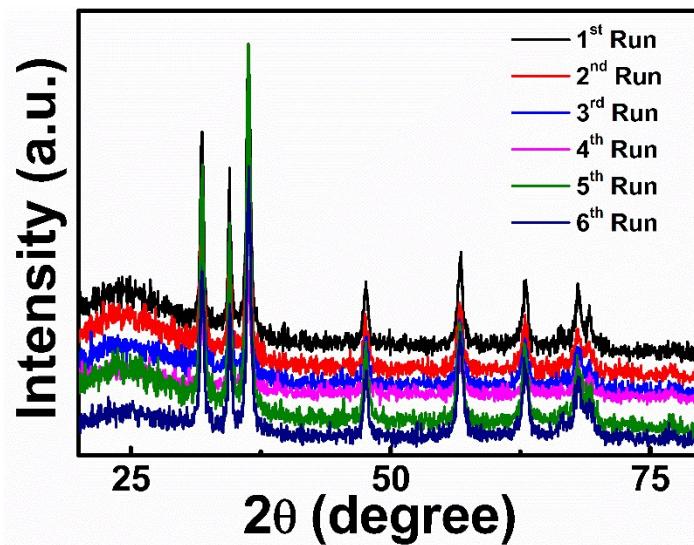
**Figure S1.** (a) Micrograph, elemental mapping of (b) Si, Zn and O together, (c) Zn (red) only, (d) Si (green) only, (e) O (blue) only and (f) energy dispersive analysis of X-rays (EDAX) of ZnO@SiO<sub>2</sub> NPs. (g) EDAX of SiO<sub>2</sub> NPs.



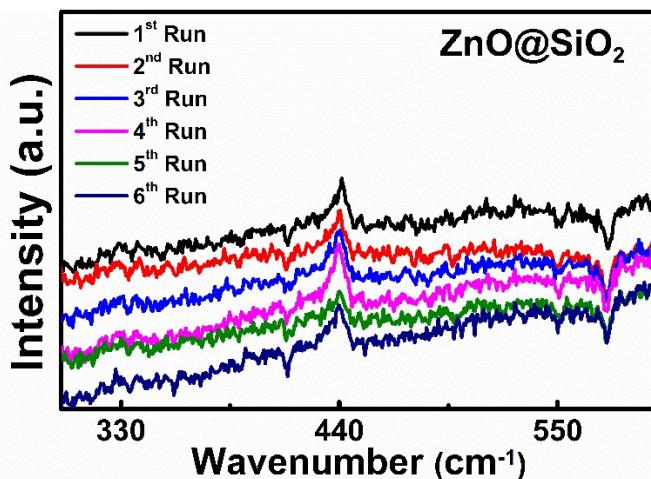
**Figure S2.** UV-Vis absorption spectra collected at an interval of 5 min up to 60 min during the synthesis of triazolo[1,2-a]indazolines using dimedone, 4-phenylurazole and 4-chlorobenzaldehyde (a) without catalyst, (b) with ZnO NPs and (c) with ZnO@SiO<sub>2</sub> NPs. Peak position wavelength  $\lambda_{\text{max}}$  of each spectrum is also indicated. Insets show the respective reactions (left) and percentage yield of product (right).



**Figure S3.** UV-Vis absorption spectra collected at an interval of 5 min up to 60 min during the synthesis of triazolo[1,2-a]indazole-triones using dimedone, 4-phenylurazole and 4-hydroxybenzaldehyde (a) without catalyst, (b) with ZnO NPs and (c) with ZnO@SiO<sub>2</sub> NPs. Peak position wavelength  $\lambda_{\text{max}} = 280 \text{ nm}$  of each spectrum is also indicated. Insets show the respective reactions (left) and percentage yield of product (right).



**Figure S4.** XRD patterns of ZnO@SiO<sub>2</sub> NPs after every use as catalyst up to six runs. They show almost no change in peak positions indicating that there is no change in the catalyst structurally. The noisy data is related to the very small quantities of the catalyst used in the experiments.



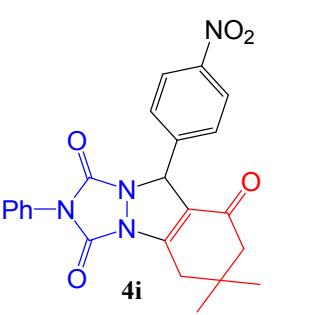
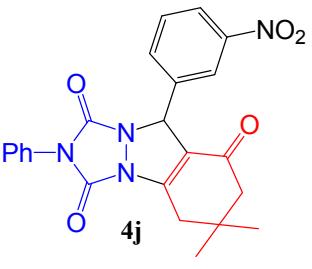
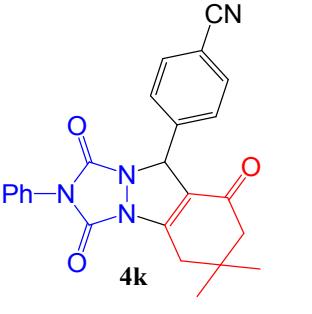
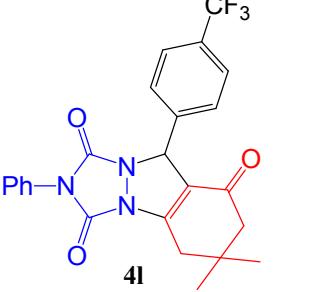
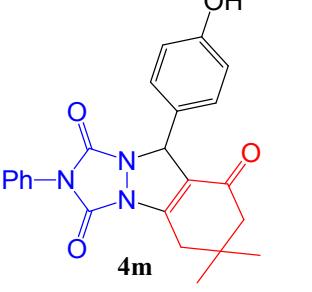
**Figure S5.** Raman spectra of  $\text{ZnO}@\text{SiO}_2$  NPs after every use as catalyst up to six runs. They show almost no change in peak positions indicating that there is no change in the catalyst structurally. The noisy data is related to the very small quantities of the catalyst used in the experiments.

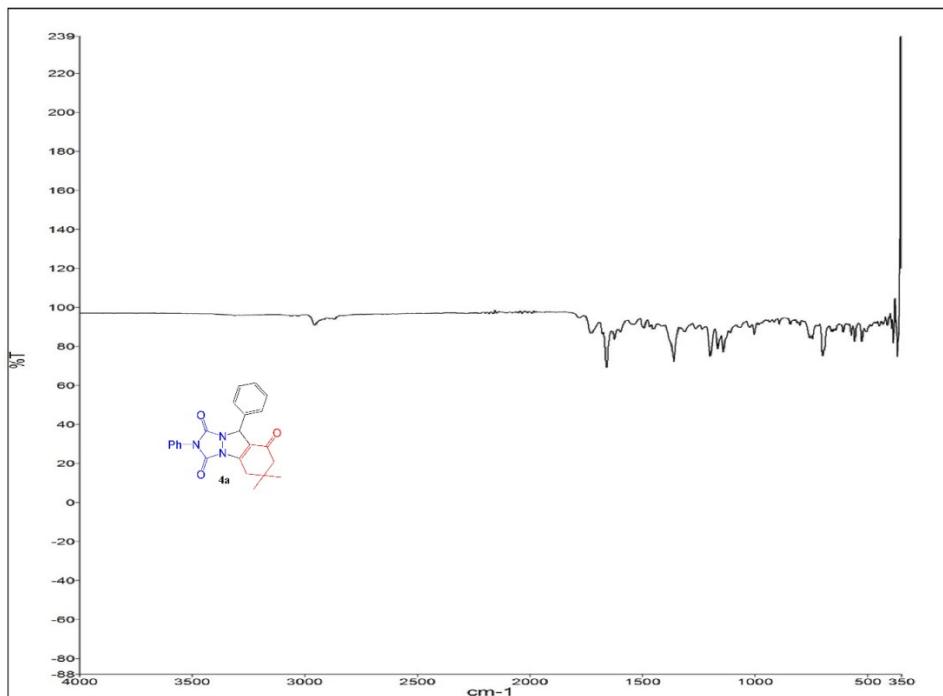
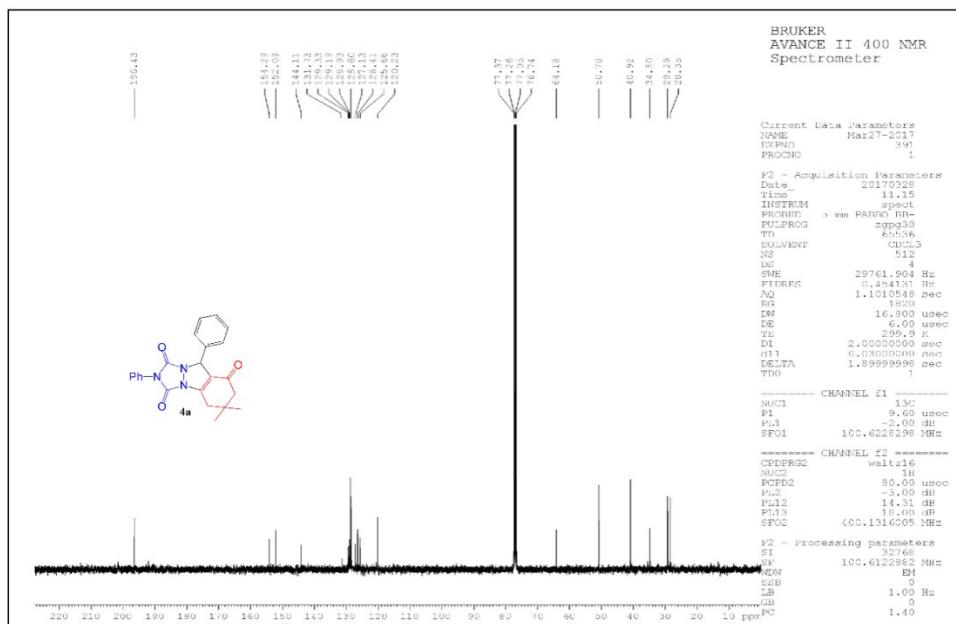
**Table S4: Spectral data**

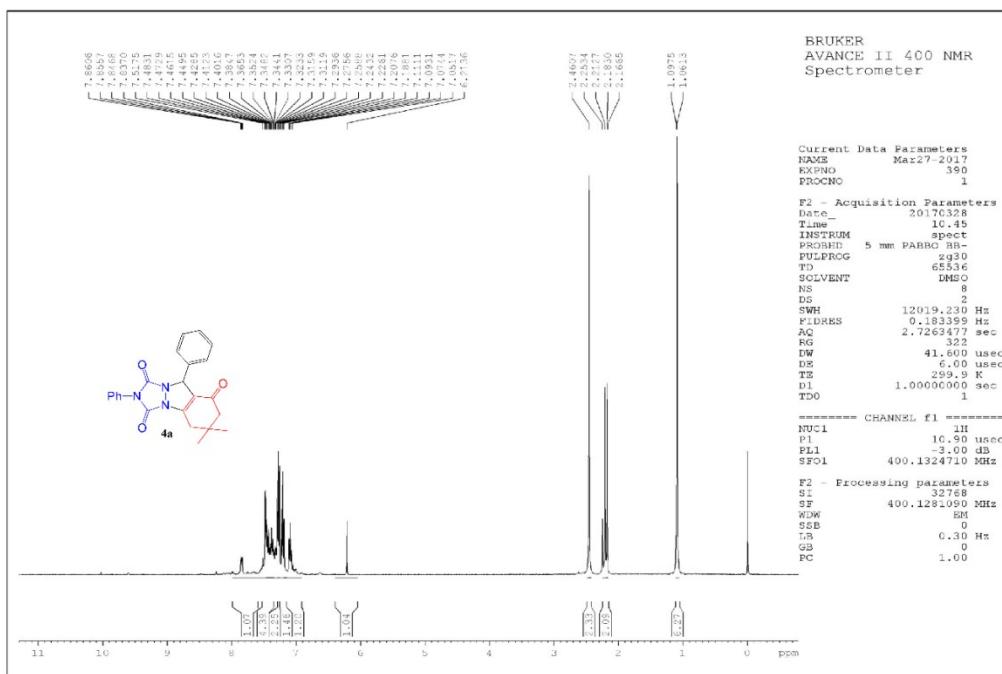
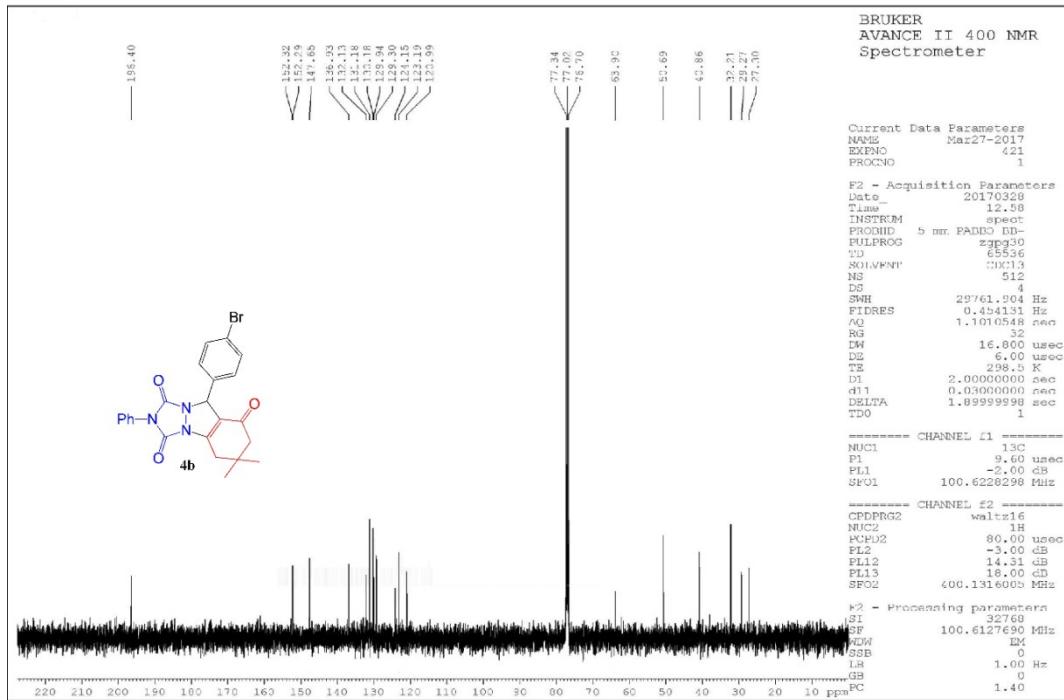
All the products were characterized by comparing their spectral (IR,  $^1\text{H}$ , and  $^{13}\text{C}$  nuclear magnetic resonance (NMR)) and physical data with those reported in the literature.<sup>1-11</sup>

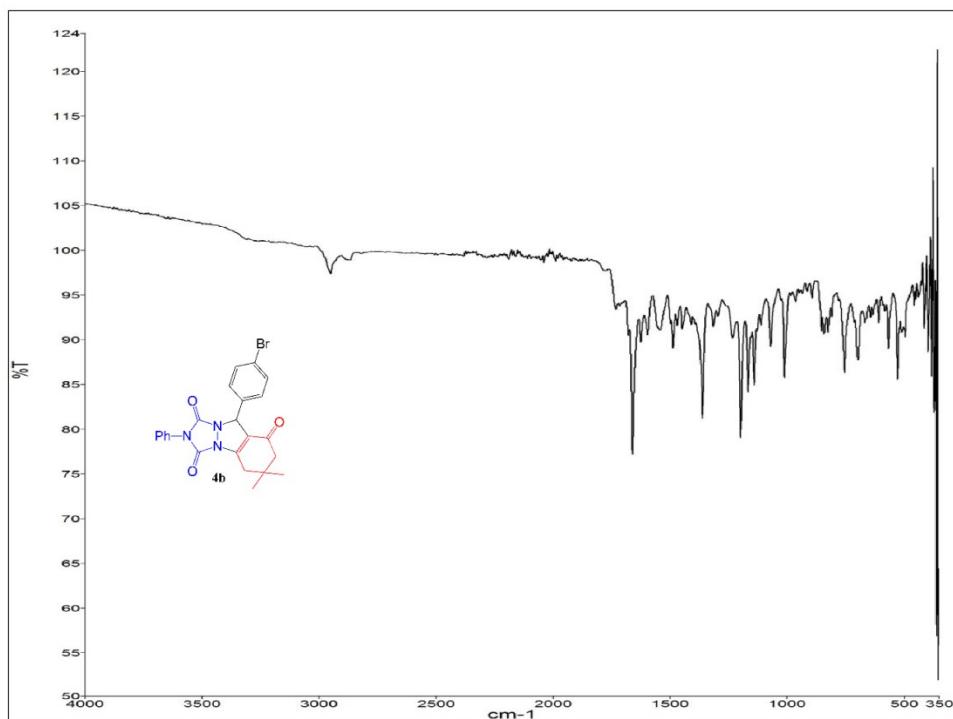
1.	6,6-Dimethyl-2,9-diphenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4a</b> , (0.174 g, 80%). White powder, mp=186-188°C, $\nu_{max}$ 3040, 2958, 1728, 1659, 1625, 1361 $\text{cm}^{-1}$ . $^1\text{H}$ NMR: $\delta$ (ppm) 1.06 (s, 3H, $\text{CH}_3$ ), 1.09 (s, 3H, $\text{CH}_3$ ), 2.16-2.25 (AB system, 2H, $\text{CH}_2$ ), 2.46 (AB System, 2H, $\text{CH}_2$ ), 6.21 (s, 1H, $\text{CH-Ph}$ ), 7.05-7.86 (10H, m, Ph). $^{13}\text{C}$ NMR: $\delta$ (ppm) 28.35, 29.29, 34.80, 40.92, 50.78, 64.18, 120.23, 125.66, 127.13, 128.60, 128.93, 129.19, 129.33, 131.73, 144.11, 152.09, 154.29, 196.43. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_3$ : C, 71.30; H, 5.46; N, 10.85%. Found: C, 71.33; H, 5.24; N, 10.89%.	
2.	9-(4-Bromophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4b</b> , (0.223 g, 85%). White powder, mp=182-184°C, $\nu_{max}$ 3050, 2953, 1732, 1660, 1625, 1380 $\text{cm}^{-1}$ . $^1\text{H}$ NMR: $\delta$ (ppm) 1.07 (s, 3H, $\text{CH}_3$ ), 1.10 (s, 3H, $\text{CH}_3$ ), 2.14-2.25 (AB System, 2H, $\text{CH}_2$ ), 2.45 (AB System, 2H, $\text{CH}_2$ ), 6.18 (s, 1H, $\text{CH-Ar}$ ), 7.10-7.60 (m, 9H, Ar). $^{13}\text{C}$ NMR: $\delta$ (ppm) 27.30, 29.27, 32.21, 40.86, 50.69, 63.90, 120.99, 123.19, 124.15, 129.30, 129.94, 131.18, 132.13, 136.93, 147.65, 152.29, 152.32, 196.40. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{BrN}_3\text{O}_3$ : C, 59.24; H, 4.32; N, 9.01%. Found: C, 59.45; H, 4.20; N, 8.80%.	
3.	9-(3-Bromophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4c</b> , (0.207 g, 79%). White powder, mp=169-170 °C, $\nu_{max}$ 3060, 2960, 1728, 1660, 1623, 1380 $\text{cm}^{-1}$ . $^1\text{H}$ NMR: $\delta$ (ppm) 1.06 (s, 3H, $\text{CH}_3$ ), 1.11 (s, 3H, $\text{CH}_3$ ), 2.12-2.29 (AB System, 2H, $\text{CH}_2$ ), 2.49 (AB System, 2H, $\text{CH}_2$ ), 6.17 (s, 1H, $\text{CH-Ar}$ ), 7.07-7.66 (m, 9H, Ar). $^{13}\text{C}$ NMR: $\delta$ (ppm) 28.12, 29.34, 35.42, 35.59, 51.67, 63.68, 120.20, 125.49, 126.20, 127.65, 129.52, 129.64, 129.97, 130.75, 132.70, 135.92, 139.53, 149.25, 151.25, 151.67, 194.23. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{BrN}_3\text{O}_3$ : C, 59.24; H, 4.32; N, 9.01%. Found: C, 59.34; H, 4.20; N, 8.80%.	

4.	9-(4-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4] triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4d</b> , (0.154 g, 65%). White powder, mp=168-170 °C, $\nu_{\text{max}}$ 3053, 2952, 1660, 1624, 1196 cm <sup>-1</sup> . <sup>1</sup> H NMR: δ (ppm) 1.10 (s, 6H, CH <sub>3</sub> ), 2.14-2.25 (AB System, 2H, CH <sub>2</sub> ), 2.46 (AB System, 2H, CH <sub>2</sub> ), 6.19 (s, 1H, CH-Ar), 7.16-7.50 (m, 9H, Ar). <sup>13</sup> C NMR: δ (ppm) 27.30, 29.27, 32.21, 40.86, 50.70, 62.12, 120.06, 128.23, 129.02, 129.77, 132.06, 134.04, 134.96, 142.69, 152.05, 152.53, 196.35. Anal. Calcd for C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>3</sub> : C, 65.48; H, 4.78; N, 9.96%. Found: C, 65.42; H, 4.26; N, 9.70%.	
5.	9-(2-Chlorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4] triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4e</b> , (0.170 g, 72%). White powder, mp=175-177 °C, $\nu_{\text{max}}$ 3052, 2953, 1720, 1660, 1620, 1382 cm <sup>-1</sup> . <sup>1</sup> H NMR: δ (ppm) 1.07 (s, 6H, CH <sub>3</sub> ), 2.18-2.25 (AB System, 2H, CH <sub>2</sub> ), 2.49 (AB System, 2H, CH <sub>2</sub> ), 6.29 (s, 1H, CH-Ar), 7.25-7.69 (m, 9H, Ar). <sup>13</sup> C NMR: δ (ppm) 28.56, 29.73, 35.20, 35.98, 51.36, 63.49, 118.79, 126.31, 127.19, 129.21, 129.86, 130.59, 131.21, 131.62, 131.67, 132.14, 133.52, 148.67, 150.24, 151.11, 192.60. Anal. Calcd for C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> O <sub>3</sub> : C, 65.48; H, 4.78; N, 9.96%. Found: C, 65.25; H, 4.22; N, 9.70%	
6.	9-(4-Fluorophenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4f</b> , (0.171 g, 75%). White powder, mp=100-102 °C, $\nu_{\text{max}}$ 3060, 2958, 1730, 1681, 1627, 1508, 1361 cm <sup>-1</sup> . <sup>1</sup> H NMR: δ (ppm) 1.02 (s, 6H, CH <sub>3</sub> ), 2.09-2.29(AB System, 2H, CH <sub>2</sub> ), 2.42 (AB System, 2H, CH <sub>2</sub> ), 6.19 (s, 1H, CH-Ar), 7.22-7.53 (m, 9H, Ar). <sup>13</sup> C NMR: δ (ppm) 28.35, 29.41, 35.21, 35.89, 51.76, 63.39, 120.27, 126.59, 129.37, 129.42, 131.25, 132.19, 137.34, 149.19, 149.25, 151.37, 151.56, 161.13, 193.5. Anal. Calcd for C <sub>23</sub> H <sub>20</sub> FN <sub>3</sub> O <sub>3</sub> : C, 68.14; H, 4.97; N, 10.36%. Found: C, 68.15; H, 5.06; N, 10.23%.	
7.	6,6-Dimethyl-2-phenyl-9-p-tolyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4g</b> , (0.185 g, 82%). White powder, mp=159-160°C, $\nu_{\text{max}}$ 3033, 2945, 1732, 1667, 1615, 1372 cm <sup>-1</sup> . <sup>1</sup> H NMR: δ (ppm) 1.12 (s, 3H, CH <sub>3</sub> ), 1.19 (s, 3H, CH <sub>3</sub> ), 2.18-2.29 (m, 5H, Ph-CH <sub>3</sub> , and CH <sub>2</sub> ), 2.32-2.47(AB System, 2H, CH <sub>2</sub> ), 6.23 (s, 1H, CH-Ar), 7.22-7.65 (m, 9H, Ar). <sup>13</sup> C NMR: δ (ppm) 21.56, 28.67, 29.21, 35.31, 35.79, 51.97, 64.34, 120.86, 126.30, 127.74, 129.61, 129.97, 130.20, 131.42, 134.32, 139.21, 139.43, 150.78, 151.92, 192.23. Anal. Calcd for C <sub>24</sub> H <sub>23</sub> N <sub>3</sub> O <sub>3</sub> : C, 71.80; H, 5.77; N, 10.47%. Found: C, 71.75; H, 5.79; N, 10.62%.	
8.	9-(4-Isopropylphenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4h</b> , (0.183 g, 76%). White powder, mp=165-166°C, $\nu_{\text{max}}$ 3056, 2959, 1710, 1661, 1622, 1418 cm <sup>-1</sup> . <sup>1</sup> H NMR: δ (ppm) 1.12 (s, 3H, CH <sub>3</sub> ), 1.20 (s, 6H, CH(CH <sub>3</sub> ) <sub>2</sub> ), 1.22 (s, 3H, CH <sub>3</sub> ), 2.15-2.25 (m, 2H, CH <sub>2</sub> ), 2.45-2.80 (m, 3H, CH <sub>2</sub> , and CH(CH <sub>3</sub> ) <sub>2</sub> ), 6.20 (s, 1H, CH-Ar), 7.05-7.49 (m, 9H, Ar). <sup>13</sup> C NMR: δ (ppm) 23.98, 27.58, 29.28, 32.31, 41.00, 51.36, 63.22, 126.23, 126.69, 128.22, 129.39, 129.76, 132.12, 135.31, 146.41, 153.52, 196.66. Anal. Calcd for C <sub>26</sub> H <sub>27</sub> N <sub>3</sub> O <sub>3</sub> : C, 72.71; H, 6.34; N, 9.78%. Found: C, 72.62; H, 6.40; N, 9.95%.	

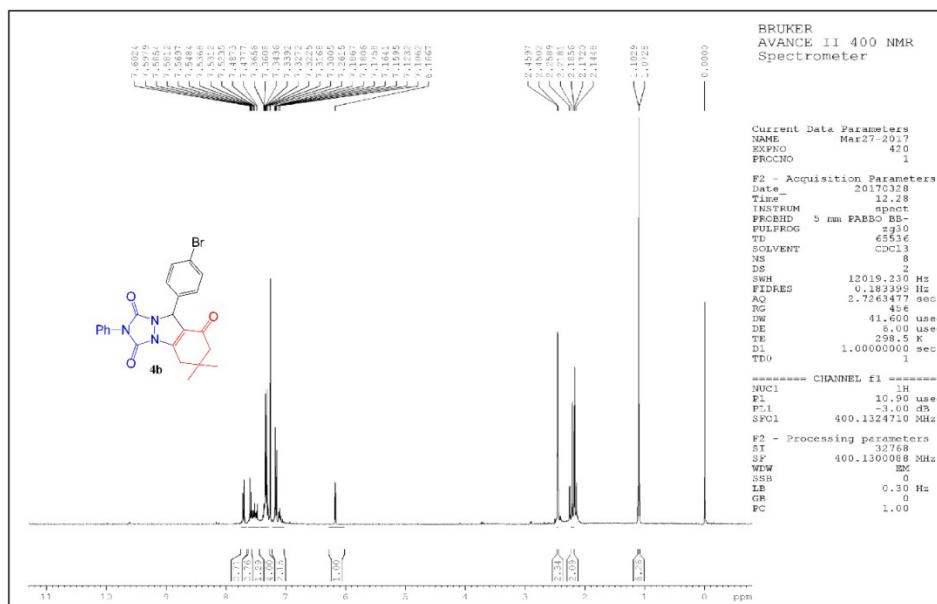
9.	<p>6,6-Dimethyl-9-(4-nitrophenyl)-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4i</b>, (0.201 g, 83%). White powder, mp=171-173 °C, <math>\nu_{\text{max}}</math> 3040, 2961, 1730, 1667, 1610, 1517, 1410, 1390, 1344 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta</math> (ppm) 1.01 (s, 3H, CH<sub>3</sub>), 1.10 (s, 3H, CH<sub>3</sub>), 2.15-2.28 (AB System, 2H, CH<sub>2</sub>), 2.42 (AB System, 2H, CH<sub>2</sub>), 6.12 (s, 1H, CH-Ar), 7.27-7.75 (m, 9H, Ar). <sup>13</sup>C NMR: <math>\delta</math> (ppm) 28.36, 29.30, 35.22, 36.80, 51.96, 63.67, 119.36, 124.25, 125.19, 128.85, 129.44, 129.98, 130.29, 144.92, 148.45, 149.66, 152.02, 152.70, 192.13. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub>: C, 63.88; H, 4.66; N, 12.96%. Found: C, 63.65; H, 4.26; N, 12.85%</p>	
10.	<p>6,6-Dimethyl-9-(3-nitrophenyl)-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4j</b>, (0.162 g, 67%). White powder, mp=129-130 °C, <math>\nu_{\text{max}}</math> 3058, 2960, 1720, 1650, 1620, 1520, 1400, 1380 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta</math> (ppm) 1.10 (s, 6H, CH<sub>3</sub>), 2.19-2.30 (AB System, 2H, CH<sub>2</sub>), 2.45 (AB System, 2H, CH<sub>2</sub>), 6.25 (s, 1H, CH-Ar), 7.17-7.80(m, 9H, Ar). <sup>13</sup>C NMR: <math>\delta</math> (ppm) 28.37, 28.69, 35.82, 36.19, 51.76, 63.26, 119.95, 122.33, 124.15, 126.20, 129.13, 129.68, 130.43, 130.89, 134.92, 139.07, 148.19, 149.36, 152.31, 192.24. Anal. Calcd for C<sub>23</sub>H<sub>20</sub>N<sub>4</sub>O<sub>5</sub>: C, 63.88; H, 4.66; N, 12.96%. Found: C, 63.75; H, 4.80; N, 12.95%.</p>	
11.	<p>4-(6,6-Dimethyl-1,3,8-trioxo-2-phenyl-1,2,3,5,6,7,8,9-octahydro-[1,2,4]triazolo[1,2-a]indazol-9-yl)benzonitrile, <b>4k</b>, (0.206 g, 89%). White powder, mp=238-240 °C, <math>\nu_{\text{max}}</math> 3045, 2956, 2210, 1730, 1710, 1672, 1610, 1370 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta</math> (ppm) 1.07 (s, 3H, CH<sub>3</sub>), 1.11 (s, 3H, CH<sub>3</sub>), 2.14-2.26 (AB System, 2H, CH<sub>2</sub>), 2.48 (AB System, 2H, CH<sub>2</sub>), 6.25 (s, 1H, CH-Ar), 7.26-7.70 (m, 9H, Ar). <sup>13</sup>C NMR: <math>\delta</math> (ppm) 27.37, 29.31, 32.31, 40.93, 50.69, 62.83, 114.72, 120.13, 125.67, 129.36, 129.98, 132.08, 138.22, 149.48, 152.68, 154.82, 196.38. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>: C, 69.89; H, 4.89; N, 13.58%. Found: C, 69.84; H, 4.70; N, 13.68%.</p>	
12.	<p>6,6-Dimethyl-2-phenyl-9-(4-(trifluoromethyl)phenyl)-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4l</b>, (0.207 g, 81%). White powder, mp=185-187 °C, <math>\nu_{\text{max}}</math> 3027, 2978, 1852, 1723, 1673, 1618, 1416, 1375, 1316, 1256, 1112 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta</math> (ppm) 1.03 (s, 6H, CH<sub>3</sub>), 2.13-2.28 (AB System, 2H, CH<sub>2</sub>), 2.58 (AB System, 2H, CH<sub>2</sub>), 6.15 (s, 1H, CH-Ar), 7.28-7.79 (m, 9H, Ar). <sup>13</sup>C NMR: <math>\delta</math> (ppm) 28.46, 29.91, 35.12, 35.59, 51.89, 63.69, 120.20, 124.32, 126.31, 126.36, 126.50, 127.29, 129.18, 129.83, 131.15, 131.60, 141.92, 149.56, 151.76, 192.13. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub>: C, 63.29; H, 4.43; N, 9.23%. Found: C, 63.23; H, 4.48; N, 9.25%.</p>	
13.	<p>9-(4-hydroxyphenyl)-6,6-dimethyl-2-phenyl-6,7-dihydro-[1,2,4]triazolo[1,2-a]indazole-1,3,8(2H,5H,9H)-trione, <b>4m</b>, (0.143 g, 63%). White powder, mp=223-225 °C, <math>\nu_{\text{max}}</math> 3200, 3052, 2952, 1660, 1624, 1197 cm<sup>-1</sup>. <sup>1</sup>H NMR: <math>\delta</math> (ppm) 1.05-1.06 (s, 6H, CH<sub>3</sub>), 2.09-2.43 (AB System, 2H, CH<sub>2</sub>), 2.45 (AB System, 2H, CH<sub>2</sub>), 6.15 (s, 1H, CH-Ar), 7.09-7.52 (m, 9H, Ar). <sup>13</sup>C NMR: <math>\delta</math> (ppm) 28.45, 28.56, 34.76, 35.39, 51.51, 62.55, 118.44, 126.65, 128.83, 128.97, 129.01, 129.36, 130.67, 134.36, 135.58, 149.22, 151.51, 151.94, 191.99. Anal. Calcd for C<sub>23</sub>H<sub>22</sub>N<sub>3</sub>O<sub>4</sub>: C, 68.31; H, 5.44; N, 10.39%. Found: C, 68.59; H, 5.88; N, 10.61%.</p>	

**Figures S6-S24. Selected spectra****Figure S7.** FTIR spectrum of product **4a**.

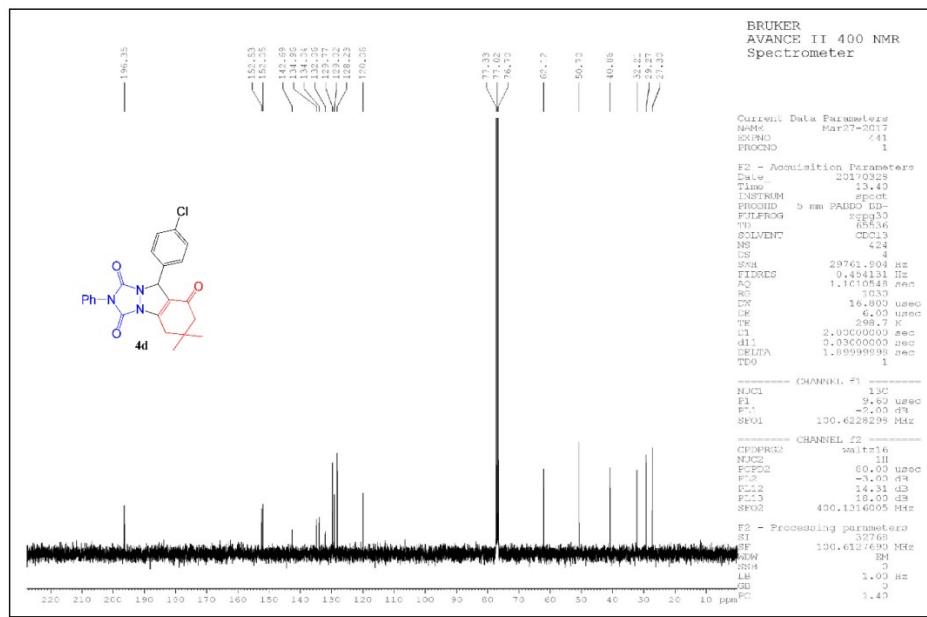
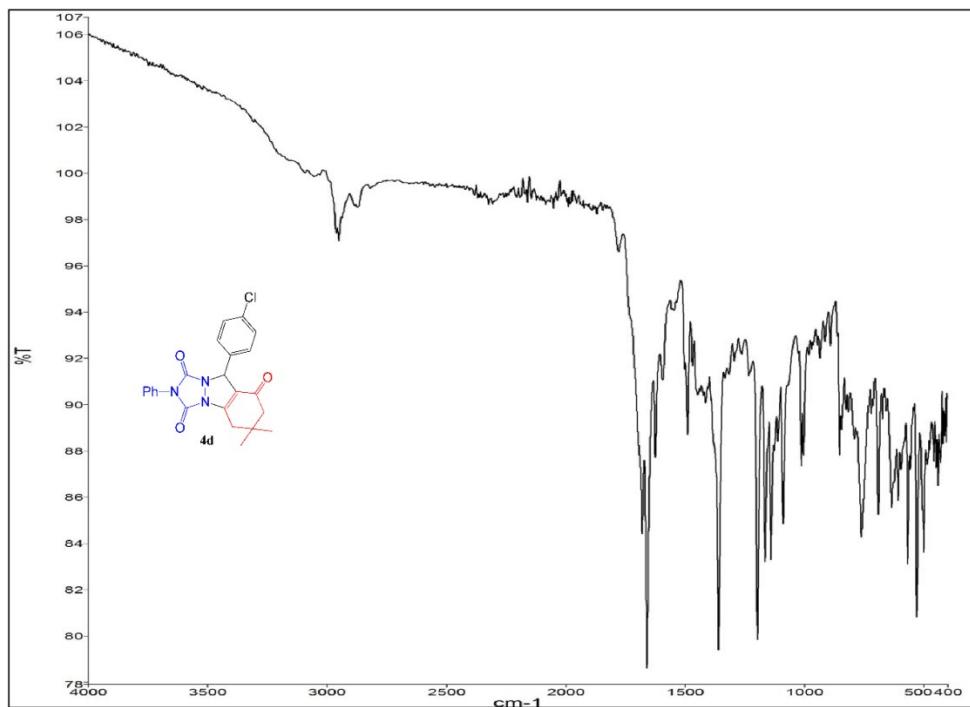
**Figure S8.** <sup>1</sup>H NMR spectrum of product **4a**.**Figure S9.** <sup>13</sup>C NMR spectrum of product **4b**.

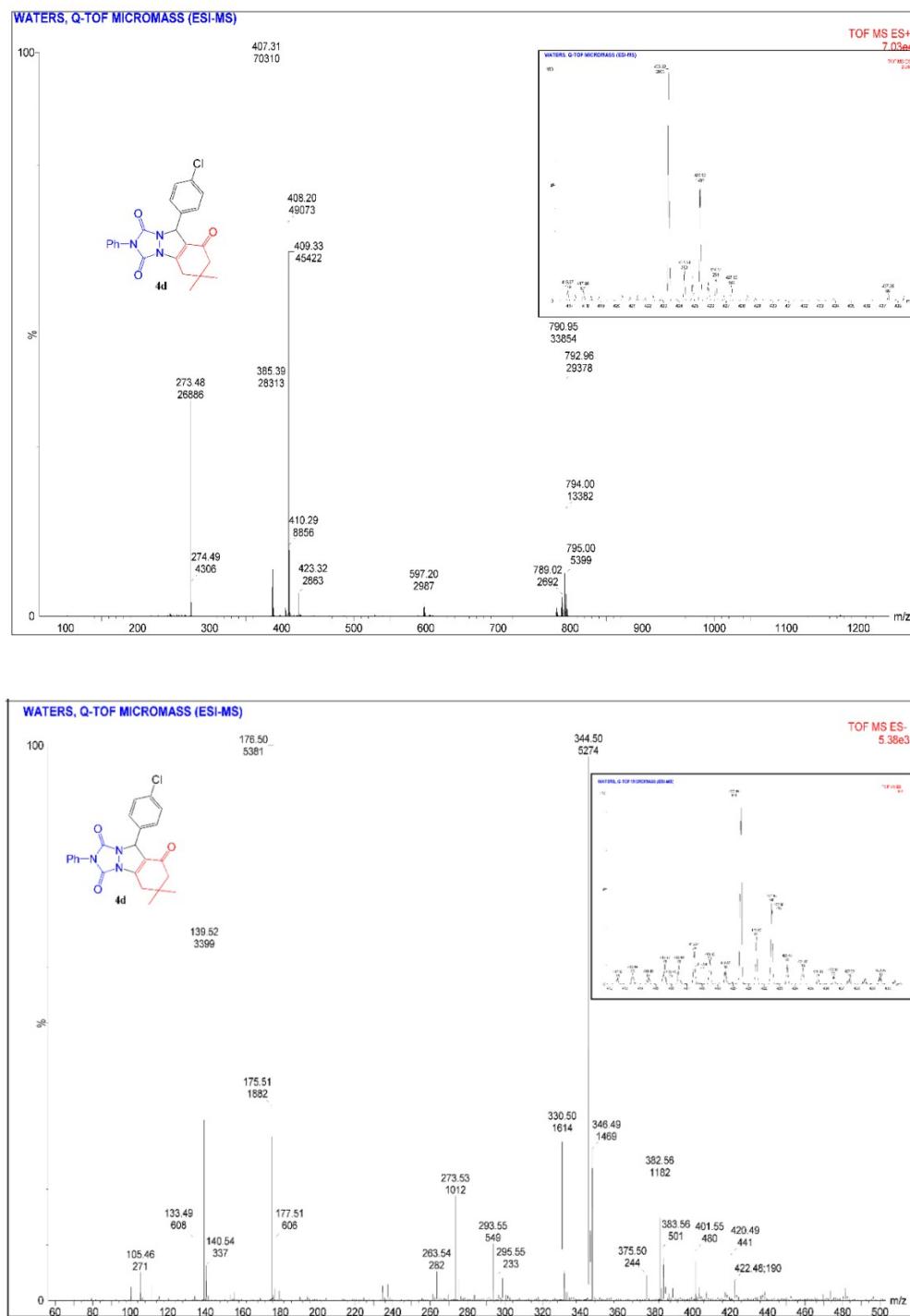


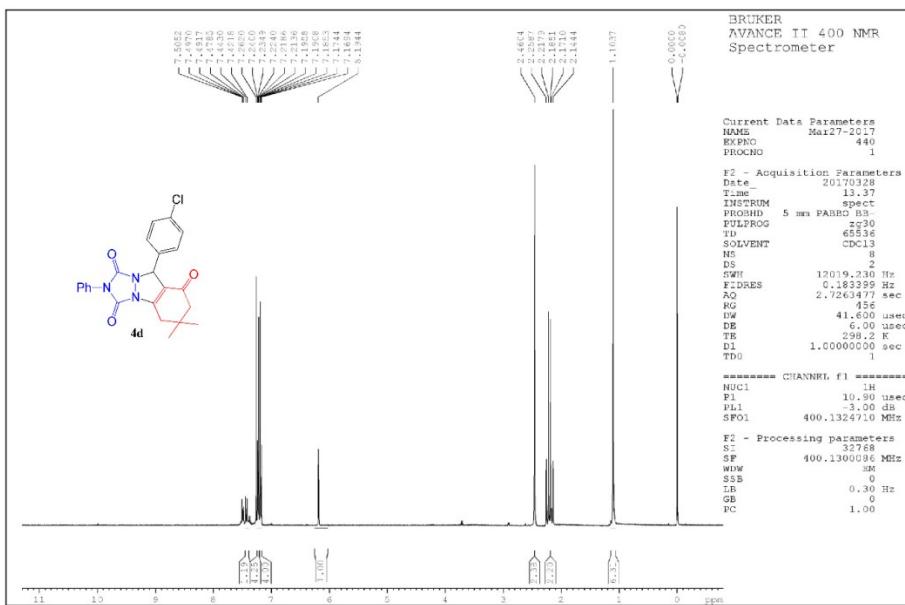
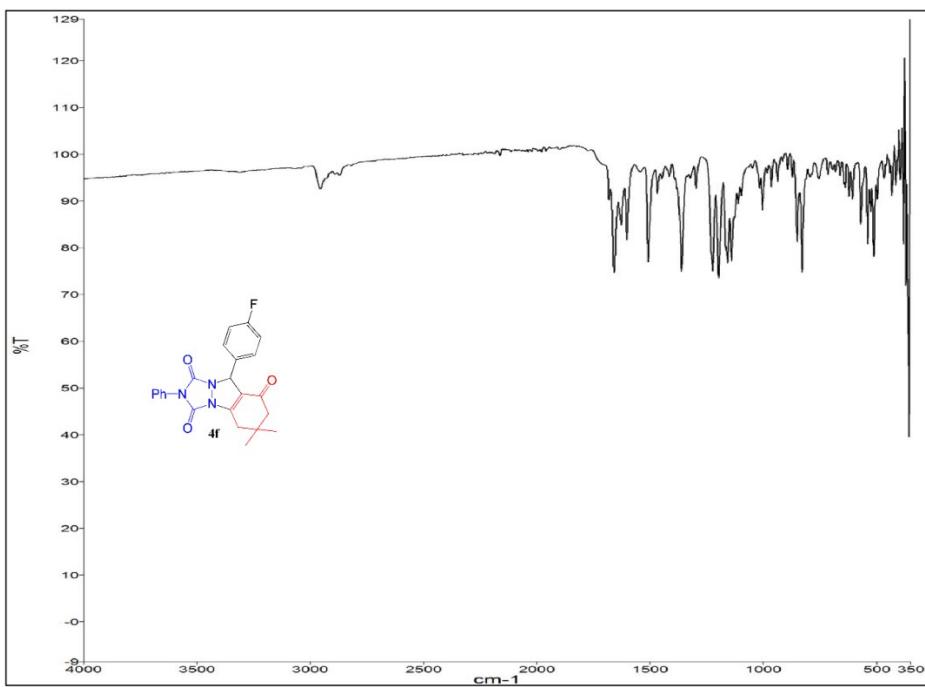
**Figure S10.** FTIR spectrum of product **4b**.

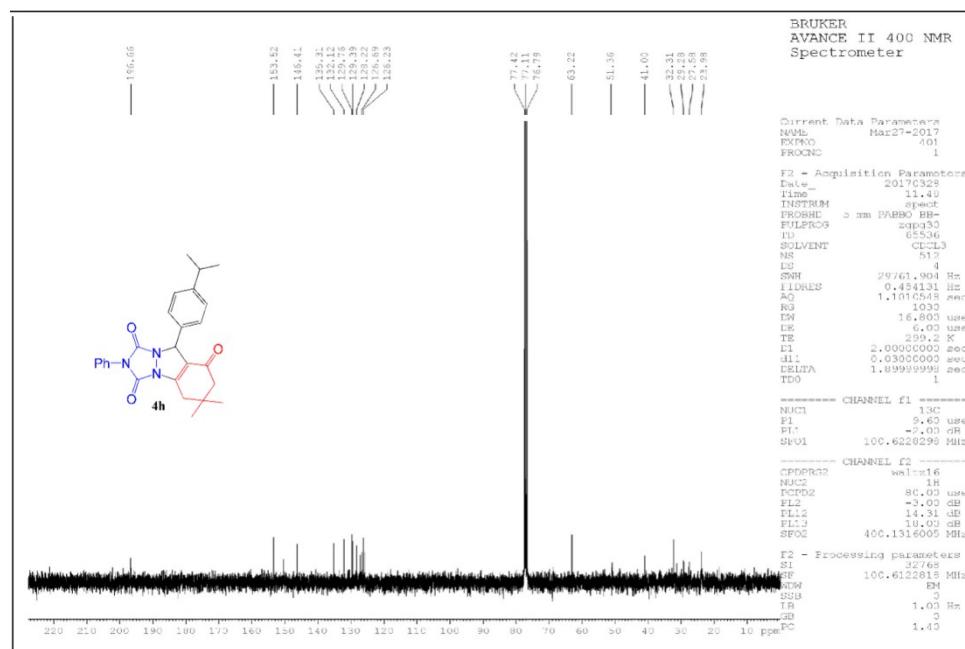
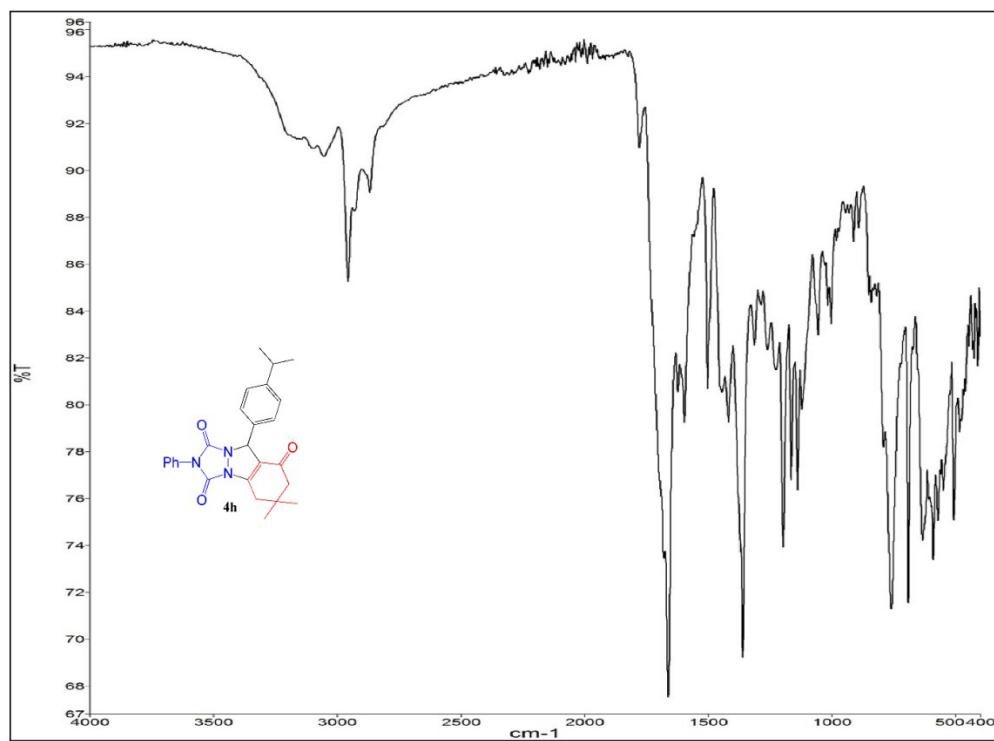


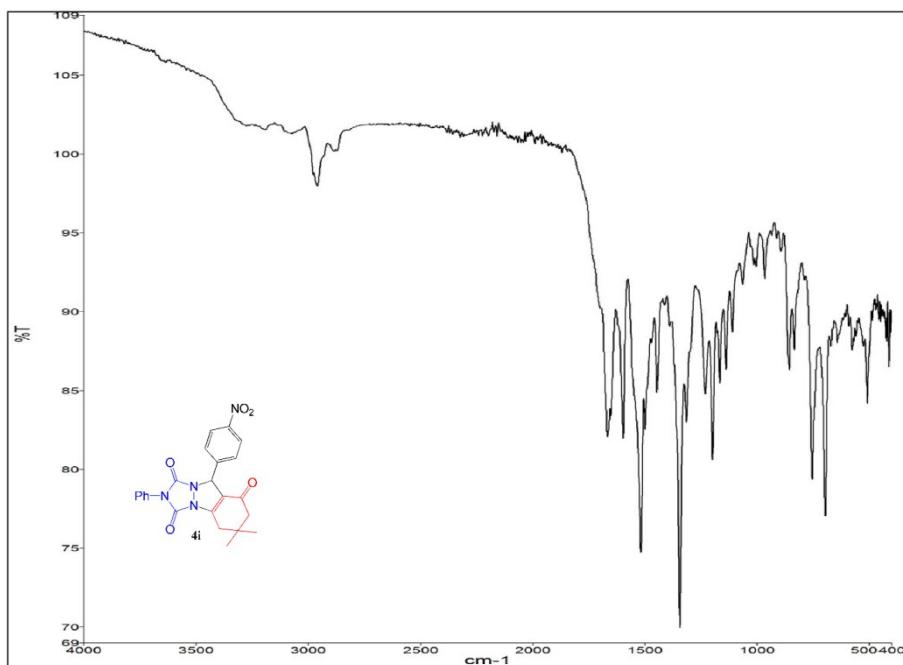
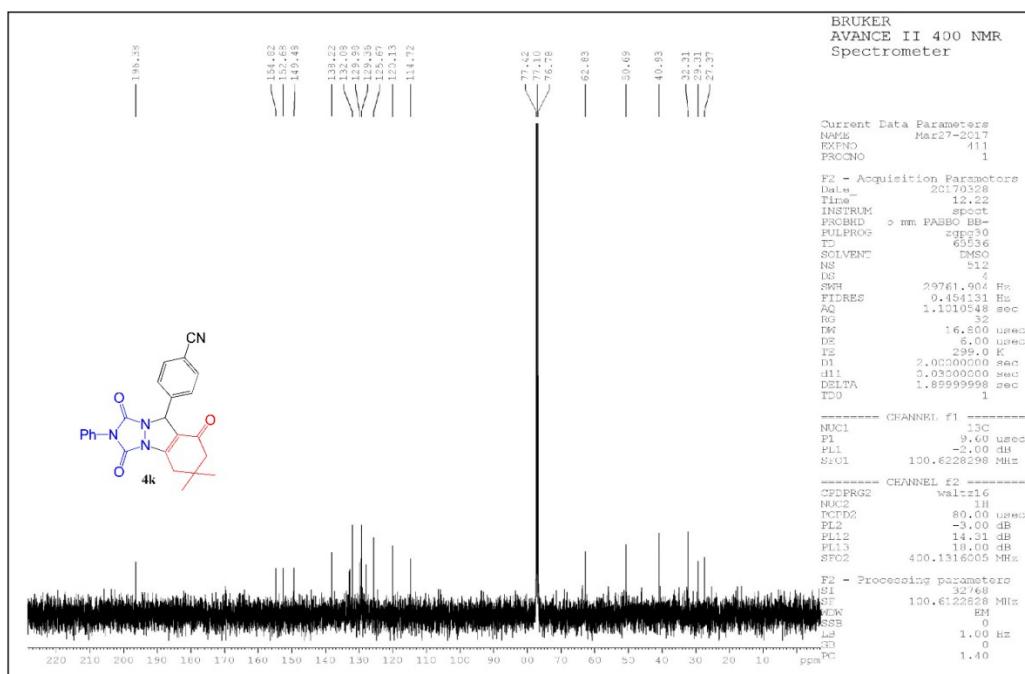
**Figure S11.**  $^1\text{H}$  NMR spectrum of product **4b**.

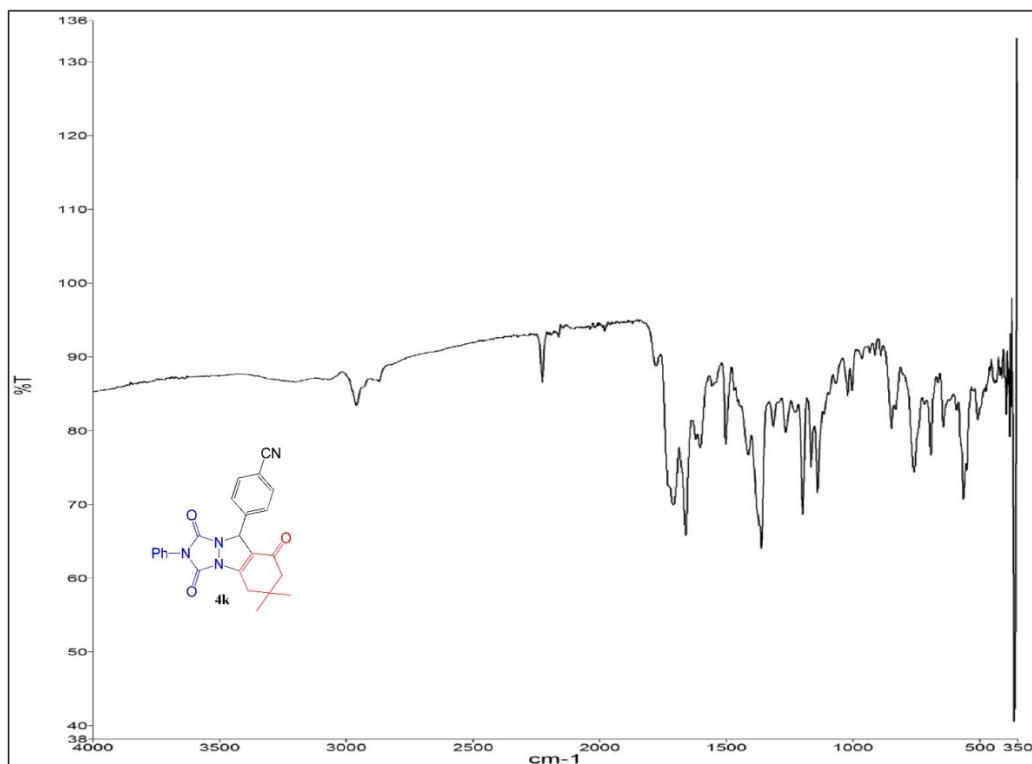
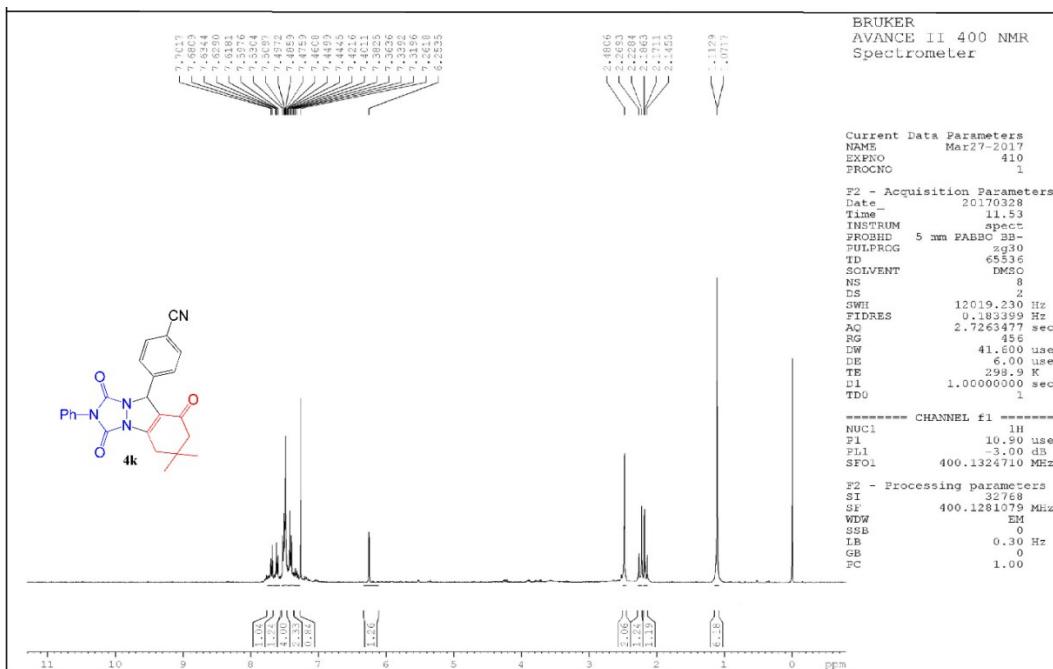
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of product **4d**.**Figure S13.** FTIR spectrum of product **4d**.

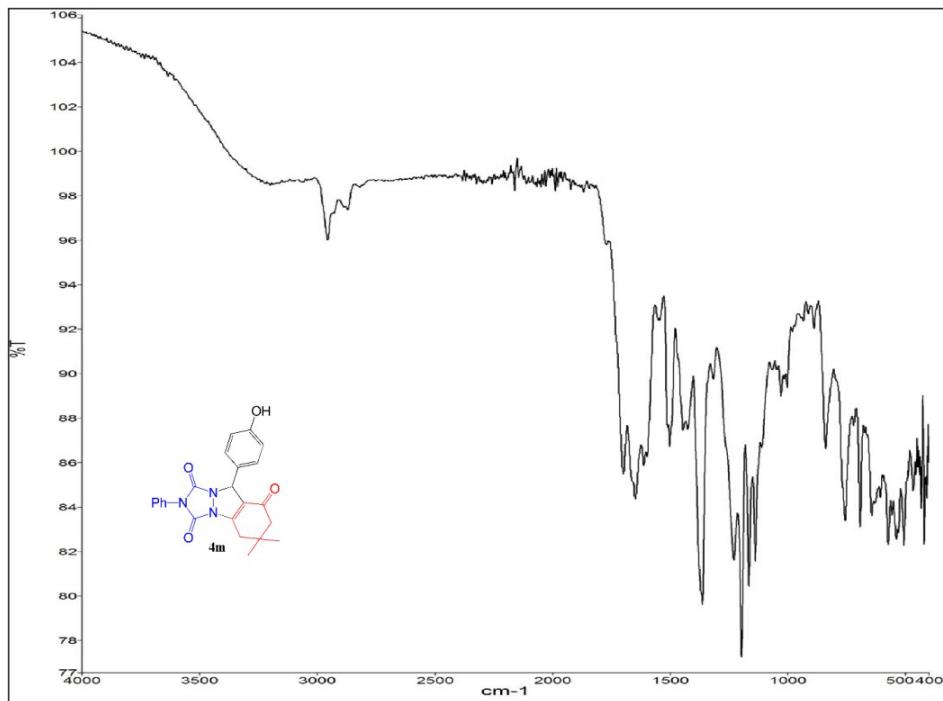
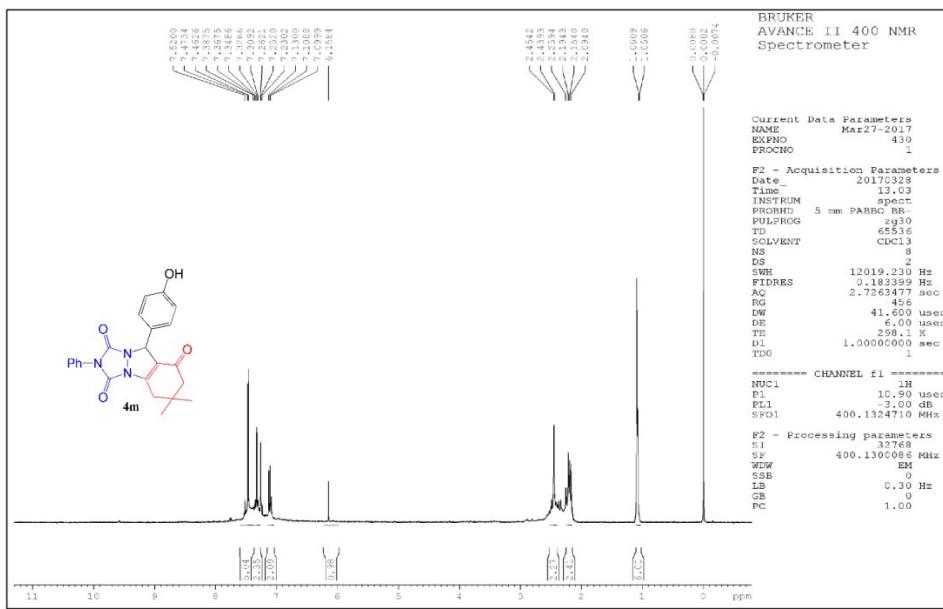
**Figure S14.** ESI-MS+ (top) and ESI-MS- (bottom) MASS spectra of product **4d**.

**Figure S15.** <sup>1</sup>H NMR spectrum of product 4d.**Figure S16.** FTIR spectrum of product 4f.

**Figure S17.** <sup>13</sup>C NMR spectrum of product 4h.**Figure S18.** FTIR spectrum of product 4h.

**Figure S19.** FTIR spectrum of product **4i**.**Figure S20.** <sup>13</sup>CNMR spectrum of product **4k**.

**Figure S21.** FTIR spectrum of product **4k**.**Figure S22.**  $^1\text{H}$  NMR spectrum of product **4k**.

**Figure S23.** FTIR spectrum of product **4m**.**Figure S24.** <sup>1</sup>H NMR spectrum of product **4m**.

## References

1. A. Bazgir, M. Seyyedhamzeh, Z. Yasaei, P. Mirzaei, *Tetrahedron Lett.* 2007, **48**, 8790.
2. A. Hasaninejad, A. Zare, M. Shekouhy, *Tetrahedron* 2011, **67**, 390.
3. H. Hamidian, S. Fozooni, A. Hassankhani, S. Z. Mohammadi, *Molecules* 2011, **16**, 9041.
4. M. Kidwai, R. Chauhan, *RSC Advan.* 2012, **2**, 7660.
5. A. Khazaei, M. A. Zolfogil, T. Faal-Rastegar, G. Chehardoli, S. Mallakpour, *Iran. J. Catal.* 2013, **3**, 211.
6. H. R. Tavakoli, S. M. Moosavi, A. Bazgir, *J. Kor. Chem. Soc.* 2013, **57**, 472.

7. S. M. Sadeghzadeh, *ChemPlusChem* 2014, **79**, 278.
8. M. Shekouhy, A. M. Sarvestani, S. Khajeh, A. K. Nezhad, *RSC Adv.* 2015, **5**, 63705.
9. D. R. Chandam, A. G. Mulik, P. P. Patil, S. D. Jagdale, D. R. Patil, M. B. Deshmukh, *Res. Chem. Intermed.* 2015, **41**, 761.
10. A. Hassankhani, E. Mosaddegh, S. Y. Ebrahimipour, *Arab. J. Chem.* 2016, **9**, S936
11. S. M. Sadeghzadeh, *RSC Adv.* 2016, **6**, 54236.