Solvent free, Ni-nanoparticles catalyzed synthesis and photophysical studies of novel 2H-indazolo[2,1-b] phthalazine-trione derivatives

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1. Experimental Section

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on Spectrum BX FT-IR, Perkin Elmer (ν_max in cm⁻¹) on KBr disks. ^1^H NMR and ^13^C NMR (400, 300 MHz and 100, 75 MHz respectively) spectra were recorded on Bruker Avance II-400 spectrometer in CDCl₃ (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on Waters ZQ-4000. Transmission Electron Microscope (TEM) was recorded on JEOL JSM 100CX. Scanning electron microscope (SEM) was recorded on JSM-6360 (JEOL). XRD was recorded on Bruker D8 XRD instrument SWAX. CHN were recorded on CHN-OS analyzer (Perkin Elmer 2400, Series II). Silica gel G (E-mark, India) was used for TLC. Hexane refers to the fraction boiling between 60 °C and 80 °C.

The organic solvents (ethylacetate and DMSO) used for the photophysical characterization were of spectroscopic grade (>99.5%) as received from Alfa Aesar. The solvent water was obtained from Elix10 water purification system (Millipore India Pvt. Ltd.). Sample concentration (0.5~1 μM) was kept sufficiently dilute to avoid any effect from aggregation and/or inner filter effect.

Steady state absorption and fluorescence emission/excitation spectra were recorded in Lambda25 and LS-55 (both from PerkinElmer Inc.) spectrometers, respectively. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively. For fluorescence emission, the sample was excited at
365 nm unless otherwise mentioned. In all the cases, 10 nm band pass was used in the excitation and 20nm for emission side.

Fluorescence quantum yields (Δf) were calculated by comparing the total fluorescence intensity (F) under the whole fluorescence spectral range with that of quinine bisulfate in 0.5 M H₂SO₄ solution (ϕᵣ = 0.546).²⁵

\[
\phi_i^f = \phi_s^f \times \frac{F_i}{F_s} \times \frac{(1 - 10^{-A_i})}{(1 - 10^{-A_s})} \times \left(\frac{n_i}{n_s}\right)^2
\]

where, \(A_i^f\) and \(A_s^f\) are the optical density of the sample and standard, respectively, and \(n_i\) is the refractive index of solvent at 293 K. The relative experimental error of the measured quantum yield was estimated within ±10%.

Fluorescence decay measurements were performed by using time correlated single photon counting (TCSPC) technique using LED based nanosecond time-resolved spectrophotometer from Photon Technology International (PTI), USA. The excitation was done at 365 nm. The instrument response function (IRF) was obtained by using a dilute colloidal suspension of dried non-dairy coffee whitener. The details of the data collection, analysis procedure for both the steady state and time-resolved measurements and method of calculation of fluorescence yield can be found elsewhere.²⁶

**General procedure**

A mixture of, dimedone 1 (2 mmol), phthalhydrazide 2 (2 mmol), aryl aldehyde 3a-n (2 mmol) and Ni NPs (10 mol %) was heated at 80 °C for the time mentioned in the table1. After completion (TLC), the reaction mixture was cooled to room temperature; 10 mL of ethyl acetate was added to dissolve to it and filtered. The filtrate was recovered and
removed in high vacuum and product was purified by column chromatography using ethyl acetate: hexane (4:6) to afford the pure products 4a-n.
Table S1: Spectral parameters of the synthesized phthalazine derivatives (4a-k) in ethyl acetate (EA) and DMSO\textsuperscript{a}.

<table>
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<tr>
<th>Products</th>
<th>Solvents</th>
<th>$\lambda_{\text{abs}}$ /nm</th>
<th>$\lambda_{\text{em}}$ /nm</th>
<th>$\varphi$</th>
<th>Decay parameters\textsuperscript{b}</th>
<th>$&lt;\tau&gt;^{c}$ /ns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{abs}}$ /nm</td>
<td>$\lambda_{\text{em}}$ /nm</td>
<td>$\varphi$</td>
<td>$\tau_1$ (a\textsubscript{1})</td>
<td>$\tau_2$ (a\textsubscript{2})</td>
</tr>
<tr>
<td>4a</td>
<td>DMSO</td>
<td>368</td>
<td>466-485</td>
<td>0.030</td>
<td>0.7 (99.8)</td>
<td>13.4 (0.2)</td>
</tr>
<tr>
<td></td>
<td>EA</td>
<td>364</td>
<td>478</td>
<td>0.006</td>
<td>0.3 (99.8)</td>
<td>4.5 (0.2)</td>
</tr>
<tr>
<td>4b</td>
<td>DMSO</td>
<td>369</td>
<td>461-485</td>
<td>0.031</td>
<td>0.6 (99.6)</td>
<td>3.0 (0.4)</td>
</tr>
<tr>
<td></td>
<td>EA</td>
<td>365</td>
<td>478</td>
<td>0.007</td>
<td>0.6 (99.7)</td>
<td>3.8 (0.3)</td>
</tr>
<tr>
<td>4c</td>
<td>DMSO</td>
<td>369</td>
<td>464-488</td>
<td>0.032</td>
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<td>5.0 (0.2)</td>
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<tr>
<td></td>
<td>EA</td>
<td>365</td>
<td>478</td>
<td>0.008</td>
<td>0.6 (99.2)</td>
<td>5.0 (0.8)</td>
</tr>
<tr>
<td>4d</td>
<td>DMSO</td>
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<td>460-483</td>
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<td>0.9 (99.8)</td>
<td>11.9(0.2)</td>
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<tr>
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<td>0.5(99.8)</td>
<td>5.2(0.2)</td>
</tr>
<tr>
<td>4e</td>
<td>DMSO</td>
<td>368</td>
<td>460-485</td>
<td>0.008</td>
<td>0.9 (99.0)</td>
<td>6.3(1.0)</td>
</tr>
<tr>
<td></td>
<td>EA</td>
<td>364</td>
<td>480</td>
<td>0.010</td>
<td>0.6(99.8)</td>
<td>6.2 (0.2)</td>
</tr>
<tr>
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<td>0.4(99.7)</td>
<td>2.4(0.3)</td>
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\textsuperscript{a}Electronic Supplementary Material (ESI) for RSC Advances

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<table>
<thead>
<tr>
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<td>368</td>
<td>460-480</td>
<td>0.017</td>
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<tr>
<td></td>
<td>EA</td>
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<td>472</td>
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<tr>
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<td>DMSO</td>
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<td>462-483</td>
<td>0.017</td>
<td>0.6(99.9)</td>
</tr>
<tr>
<td></td>
<td>EA</td>
<td>364</td>
<td>470</td>
<td>0.006</td>
<td>1.0(99.7)</td>
</tr>
<tr>
<td>4i</td>
<td>DMSO</td>
<td>368</td>
<td>461-483</td>
<td>0.054</td>
<td>0.9(99.8)</td>
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<tr>
<td></td>
<td>EA</td>
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<td>477</td>
<td>0.010</td>
<td>0.4(99.9)</td>
</tr>
<tr>
<td>4j</td>
<td>DMSO</td>
<td>369</td>
<td>458-485</td>
<td>0.024</td>
<td>0.5(99.8)</td>
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<td>0.005</td>
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</tr>
<tr>
<td>4k</td>
<td>DMSO</td>
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<td>458-485</td>
<td>0.017</td>
<td>0.5(99.5)</td>
</tr>
<tr>
<td></td>
<td>EA</td>
<td>363</td>
<td>472</td>
<td>0.020</td>
<td>0.6(99.8)</td>
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</tbody>
</table>

^a\(\lambda_{abs}\) = absorbance maxima, \(\lambda_{abs}\) = emission maxima, \(\phi\) = quantum yield, ^bthe measured values are within ±0.1 ns; ^ccalculated from equation (1b)
Spectral Data

1. **Compound 4a**

Yellow solid. IR (KBr): 2965, 2375, 1666 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.28-8.17\) (m, 2H), 7.79-7.75 (m, 2H), 7.34-7.19 (m, 5H), 6.37 (s, 1H), 3.36-3.13 (AB system, \(J = 18.4\) Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). ESI-MS: \(m/\epsilon\) 373 [M + H]\(^+\). Anal. Calcd for C\(_{23}\)H\(_{20}\)N\(_2\)O\(_3\): C, 74.18; H, 5.41; N, 7.52. Found: C, 74.07; H, 5.35; N, 7.35.

2. **Compound 4b**

Yellow solid. IR (KBr): cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.28-8.18\) (m, 2H), 7.78-7.76 (m, 2H), 7.23 7.07 (d, \(J = 7.6\) Hz, 2H), 6.34 (s, 1H), 3.36-3.13 (AB system, \(J = 18.2\) Hz, 2H), 2.22 (s, 3H), 1.13 (s, 6H). ESI-MS: \(m/\epsilon\) 387 [M + H]\(^+\). Anal. Calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_3\): C, 74.59; H, 5.74; N, 7.25. Found: C, 74.51; H, 5.80; N, 7.08.

3. **Compound 4c**

Yellow solid. IR (KBr): 2963, 2376, 1660 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.28-8.18\) (m, 2H), 7.78-7.75 (m, 2H), 7.28 (d, \(J = 8.8\) Hz, 2H), 6.79 (d, \(J = 8.4\) Hz, 2H), 6.34 (s, 1H), 3.69 (s, 3H), 3.37-3.13 (AB system, \(J = 19.2\) Hz, 2H), 2.27 (s, 2H), 1.15 (s, 3H), 1.13 (s, 3H). ESI-MS: \(m/\epsilon\) 403 [M + H]\(^+\). Anal. Calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_4\): C, 71.63; H, 5.51; N, 6.96. Found: C, 71.83; H, 5.65; N, 6.87.
4. **Compound 4d**

Yellow solid. IR (KBr): 2966, 2375, 1665 cm\(^{-1}\) \(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.31-8.17\) (m, 2H), 7.82-7.79 (m, 2H), 7.58 (d, \(J = 8.4\) Hz, 2H), 7.48 (d, \(J = 8.4\) Hz, 2H), 6.38 (s, 1H), 3.34-3.15 (AB system, \(J = 19.2\) Hz, 2H), 2.26 (s, 2H), 1.14 (s, 3H), 1.11 (s, 3H). 

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 191.0, 154.9, 153.5, 150.5, 140.5, 133.7, 132.9, 131.5, 127.9, 127.6, 127.1, 126.8, 126.7, 117.4, 116.3, 111.5, 63.3, 49.7, 37.0, 33.7, 27.6, 27.3.

ESI-MS: \(m/z\) 398 [M + H]\(^{+}\). Anal. Calcd for C\(_{24}\)H\(_{19}\)N\(_3\)O\(_3\): C, 72.53; H, 4.82; N, 10.57. Found: C, 72.71; H, 4.70; N, 10.73.

5. **Compound 4e**

Yellow solid. IR (KBr): 2965, 2375, 1666 cm\(^{-1}\) \(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.29-8.08\) (m, 4H), 7.80-7.79 (m, 2H), 7.53 (d, \(J = 8.4\) Hz, 2H), 6.41 (s, 1H), 3.35-3.15 (AB system, \(J = 19.2\) Hz, 2H), 2.25 (s, 2H), 1.13 (s, 3H), 1.10 (s, 3H). 

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 192.1, 155.9, 154.5, 151.7, 147.8, 143.4, 134.8, 133.9, 128.9, 128.5, 128.2, 128.0, 127.7, 124.0, 117.2, 64.1, 50.7, 37.9, 34.7, 28.6, 28.3. ESI-MS: \(m/z\) 418 [M + H]\(^{+}\). Anal. Calcd for C\(_{23}\)H\(_{19}\)N\(_3\)O\(_5\): C, 66.18; H, 4.59; N, 10.07. Found: C, 65.90; H, 4.45; N, 10.23.

6. **Compound 4f**

Yellow solid. IR (KBr): 2939, 2229, 1666 cm\(^{-1}\) \(^{1}\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.29-8.18\) (m, 2H), 7.80-7.78 (m, 2H), 7.30 (d, \(J = 8.8\) Hz, 2H), 7.24 (d, \(J = 8.4\) Hz, 2H), 6.34 (s, 1H), 3.35-3.13 (AB system, \(J = 18.2\) Hz, 2H), 2.26 (s, 2H), 1.13 (s, 6H). 

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta = 192.1, 156.0, 154.3, 151.1, 134.9, 134.6, 134.5, 133.6, 128.97, 128.93, 128.91, 128.5, 128.0, 127.7, 118.0, 64.3, 50.8, 38.0, 34.6, 28.6, 28.4. ESI-MS:
m/z 407, 409 [M + H]^+. Anal. Calcd for C_{23}H_{19}ClN_{2}O_{3}: C, 67.90; H, 4.71; N, 6.89. Found: C, 68.17; H, 4.87; N, 6.98.

7. **Compound 4g**

Yellow solid. IR (KBr): cm⁻¹. \(^1\)H NMR (CDCl₃, 400 MHz) \(\delta = 8.29-8.18\) (m, 2H), 7.80-7.78 (m, 2H), 7.40 (d, \(J = 8.4\) Hz, 2H), 7.23 (d, \(J = 8.4\) Hz, 2H), 6.32 (s, 1H), 3.35-3.13 (AB system, \(J = 18.2\) Hz, 2H), 2.26 (s, 2H), 1.13 (s, 3H), 1.30 (s, 3H). \(^{13}\)C NMR (CDCl₃, 100 MHz) \(\delta = 192.1, 156.0, 154.3, 151.1, 135.4, 134.6, 133.7, 131.9, 128.9, 128.89, 128.82, 128.0, 127.7, 122.7, 118.0, 64.4, 50.8, 38.0, 34.6, 28.6, 28.4. ESI-MS: m/z 451, 453 [M + H]^+. Anal. Calcd for C_{23}H_{19}BrN_{2}O_{3}: C, 61.21; H, 4.24; N, 6.21. Found: C, 61.40; H, 4.12; N, 6.48.

8. **Compound 4h**

Yellow solid. IR (KBr): 2965, 2369, 1666 cm⁻¹. \(^1\)H NMR (CDCl₃, 400 MHz) \(\delta = 8.28-8.18\) (m, 2H), 7.80-7.78 (m, 2H), 7.34-7.31 (m, 2H), 6.97 (t, \(J = 8.2\) Hz, 2H), 6.36 (s, 1H), 3.36-3.14 (AB system, \(J = 18.8\) Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). ESI-MS: m/z 391 [M + H]^+. Anal. Calcd for C_{23}H_{19}FN_{2}O_{3}: C, 70.76; H, 4.91; N, 7.18. Found: C, 70.65; H, 4.88; N, 7.30.

9. **Compound 4i**

Yellow solid. IR (KBr): 2959, 2362, 1666 cm⁻¹. \(^1\)H NMR (CDCl₃, 400 MHz) \(\delta = 8.30-8.19\) (m, 2H), 7.81-7.78 (m, 2H), 7.30-7.19 (m, 4H), 6.33 (s, 1H), 3.35-3.15 (AB system, \(J = 18.6\) Hz, 2H), 2.27 (s, 2H), 1.14 (s, 6H). Anal. Calcd for C_{23}H_{19}ClN_{2}O_{3}: C, 67.90; H, 4.71; N, 6.89. Found: C, 67.61; H, 4.56; N, 7.15.
10. **Compound 4j**

Yellow solid. IR (KBr): cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.30-8.16\) (m, 2H), 7.79-7.77 (m, 2H), 7.41-7.14 (m, 4H), 6.60 (s, 1H), 3.35-3.14 (AB system, \(J = 18.0\) Hz, 2H), 2.25 (s, 2H), 1.14 (s, 6H). ESI- MS: \(m/z\) 407, 409 [M + H]\(^+\). Anal. Calcd for C\(_{23}\)H\(_{19}\)ClN\(_2\)O\(_3\): C, 67.90; H, 4.71; N, 6.89. Found: C, 67.93; H, 4.77; N, 6.71.

11. **Compound 4k**

Yellow solid. IR (KBr): 2960, 2382, 1666 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 8.32-8.08\) (m, 4H), 7.83-7.82 (brs, 3H), 7.51-7.47 (m, 1H), 6.45 (s, 1H), 3.38-3.18 (AB system, \(J = 18.7\) Hz, 2H), 2.28 (s, 2H), 1.15 (s, 6H). ESI- MS: \(m/z\) 418 [M + H]\(^+\). Anal. Calcd for C\(_{23}\)H\(_{19}\)N\(_3\)O\(_5\): C, 66.18; H, 4.59; N, 10.07. Found: C, 66.37; H, 4.47; N, 10.34.

12. **Compound 4l**

Yellow solid. IR (KBr): 2965, 2372, 1666 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 8.37-8.24\) (m, 4H), 7.87-7.13 (m, 4H), 6.71 (s, 1H), 3.43-3.21 (AB system, \(J = 19.2\) Hz, 2H), 2.32 (s, 2H), 1.25 (s, 3H), 1.21 (s, 3H). ESI- MS: \(m/z\) 451, 453 [M + H]\(^+\). Anal. Calcd for C\(_{23}\)H\(_{19}\)BrN\(_2\)O\(_3\): C, 61.21; H, 4.24; N, 6.21. Found: C, 61.10; H, 4.10; N, 6.24.

13. **Compound 4m**
Yellow solid. IR (KBr): 2965, 2375, 1666 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 8.27-8.24\) (m, 4H), 7.88-6.98 (m, 4H), 6.53 (s, 1H), 3.45-3.18 (AB system, \(J = 18.0\) Hz, 2H), 2.33 (s, 2H), 1.25 (s, 3H), 1.92 (s, 3H). ESI- MS: \(m/z\) 391 [M + H]^+. Anal. Calcd for C\(_{23}\)H\(_{19}\)FN\(_2\)O\(_3\): C, 70.76; H, 4.91; N, 7.18. Found: C, 70.71; H, 5.14; N, 7.06.

14. Compound 4n

![Image](image_url)

Yellow solid. IR (KBr): 2966, 2375, 1665 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 8.35-8.25\) (m, 4H), 7.90-7.84 (m, 4H), 6.39 (s, 1H), 3.44-3.20 (AB system, \(J = 17.5\) Hz, 2H), 2.34 (s, 2H), 1.21 (s, 6H). ESI- MS: \(m/z\) 398 [M + H]^+. Anal. Calcd for C\(_{23}\)H\(_{19}\)BrN\(_2\)O\(_3\): C, 61.21; H, 4.24; N, 6.21. Found: C, 60.93; H, 4.12; N, 6.30.
3. $^1$H and $^{13}$C NMR spectra

1. Compound 4a

$^1$H NMR Spectra of Compound 4a
2. Compound 4b

$^1H$ NMR Spectra of Compound 4b
3. Compound 4c

$^1$H NMR Spectra of Compound 4c
4. Compound 4d

$^1$H NMR Spectra of Compound 4d
5. Compound 4d

$^{13}$C NMR Spectra of Compound 4d

Electronic Supplementary Material (ESI) for RSC Advances
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6. Compound 4e

$^1$H NMR Spectra of Compound 4e
7. Compound 4e

$^{13}$C NMR Spectra of Compound 4e
8. Compound 4f

$^1$H NMR Spectra of Compound 4f
9. Compound 4f

$^{13}$C NMR Spectra of Compound 4f
10. Compound 4g

\(^1\)H NMR Spectra of Compound 4g
11. Compound 4g

$^{13}$C NMR Spectra of Compound 4g
12. Compound 4h

\(^1\)H NMR Spectra of Compound 4h
13. Compound 4i

$^1$H NMR Spectra of Compound 4i
14. Compound 4j

$^1$H NMR Spectra of Compound 4j
15. Compound 4k

$^1\text{H NMR Spectra of Compound 4k}$
16. Compound 4l

$^1$H NMR Spectra of Compound 4l
17. Compound 4m

$^1$H NMR Spectra of Compound 4m
18. Compound 4n

$^1$H NMR Spectra of Compound 4n