

# Supporting Information

## A direct synthesis method towards spirocyclic indazole derivatives via Rh(III)-catalyzed C–H activation and spiroannulation

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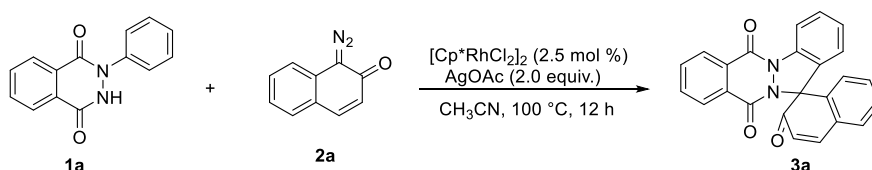
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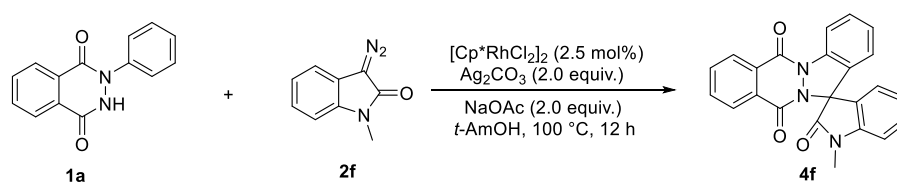
## 1. General information.

All commercials obtained from commercial sources were used as received unless otherwise noted. Substrate **1**<sup>[1]</sup> and **2**<sup>[2, 3]</sup> were prepared by literature reports. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. NMR spectra were recorded on 400 MHz or 600 MHz spectrometers in the solvent indicated. Chemical shifts are reported downfield from TMS ( $\delta = 0$ ) for <sup>1</sup>H NMR. For <sup>13</sup>C NMR, chemical shifts are reported in the scale relative to CDCl<sub>3</sub> ( $\delta = 77.0$ ). <sup>19</sup>F NMR were recorded on Bruker Ascend™ (376 MHz). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

## 2. General procedure for Rh(III)-Catalyzed [4 + 1] annulation of diazo compounds with 2-phenyl-2,3-dihydrophthalazine-1,4-dione.



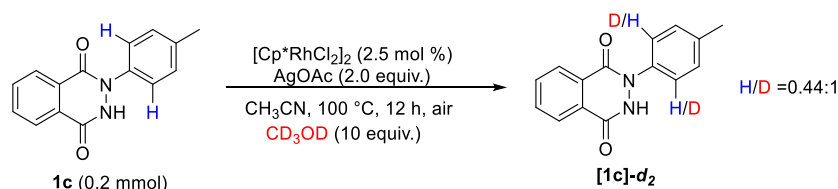
Synthesis of **3a** is representative. 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol), 1-diazonaphthalen-2(1H)-one **2a** (51.1 mg, 0.30 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (3.1 mg, 0.005 mmol) and AgOAc (66.8 mg, 0.40 mmol), were dissolved in  $\text{CH}_3\text{CN}$  (2.0 mL). The mixture was stirred at 100 °C under air for 12 hours. The resulting mixture was cooled to room temperature and then diluted with dichloromethane (20 mL). The suspension was then transferred to a round bottom flask (50 mL), concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to give **3a** (68.9 mg, 91%) as a white solid.



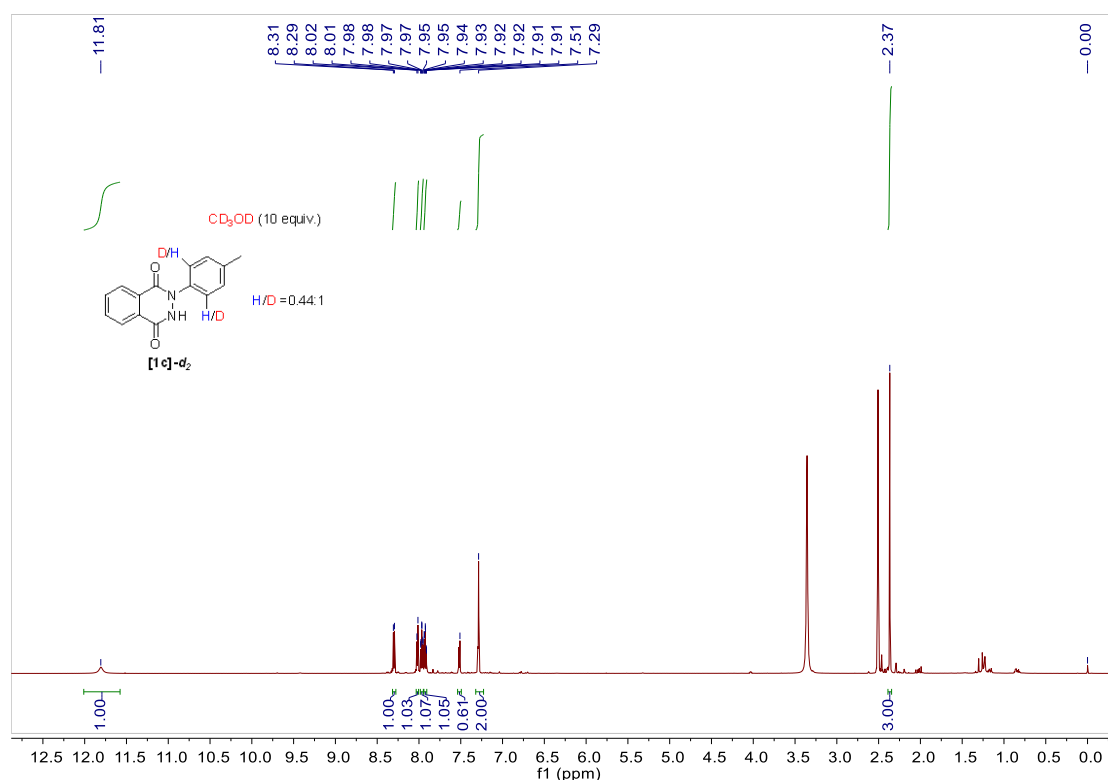
Synthesis of **4f** is representative. 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol), 3-diazo-1-methylindolin-2-one **2f** (51.9 mg, 0.30 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (110.3 mg, 0.40 mmol) and NaOAc (32.8 mg, 0.40 mmol) were dissolved in *t*-AmOH (2.0 mL). The mixture was stirred at 100 °C under air for 12 hours. The resulting mixture was cooled to room temperature and then diluted with dichloromethane (20 mL). The suspension was then transferred to a round bottom flask (50 mL), concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 2/1) to give **3a** (42.0 mg, 55%) as a white solid.

### 3. Isotope labeling experiments

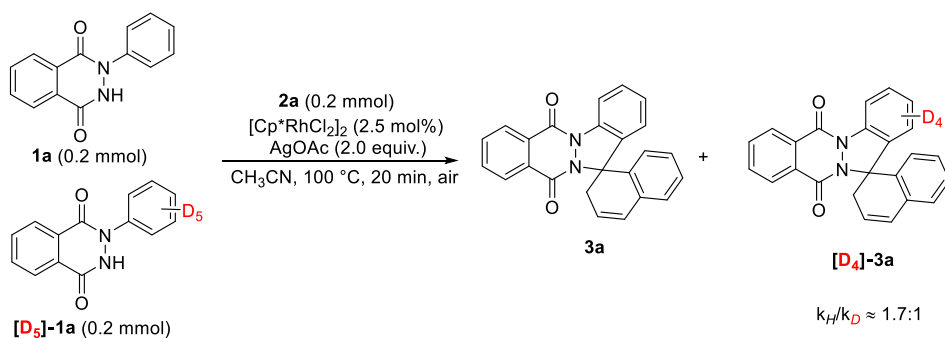
#### 3.1 H/D exchange experiment



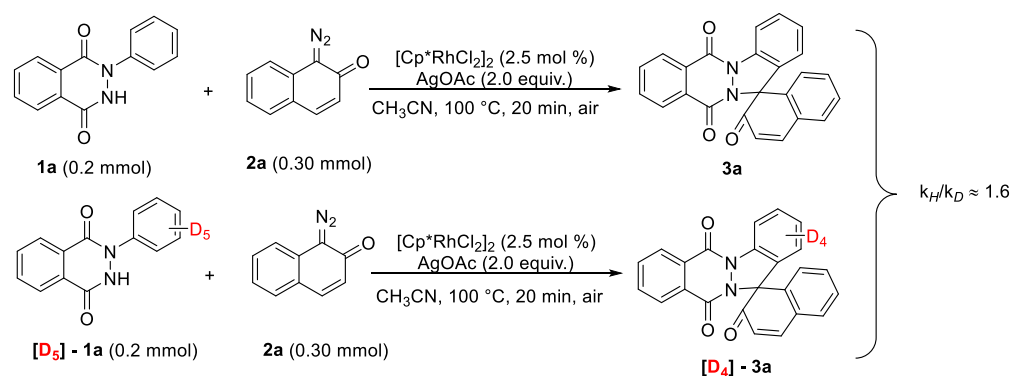
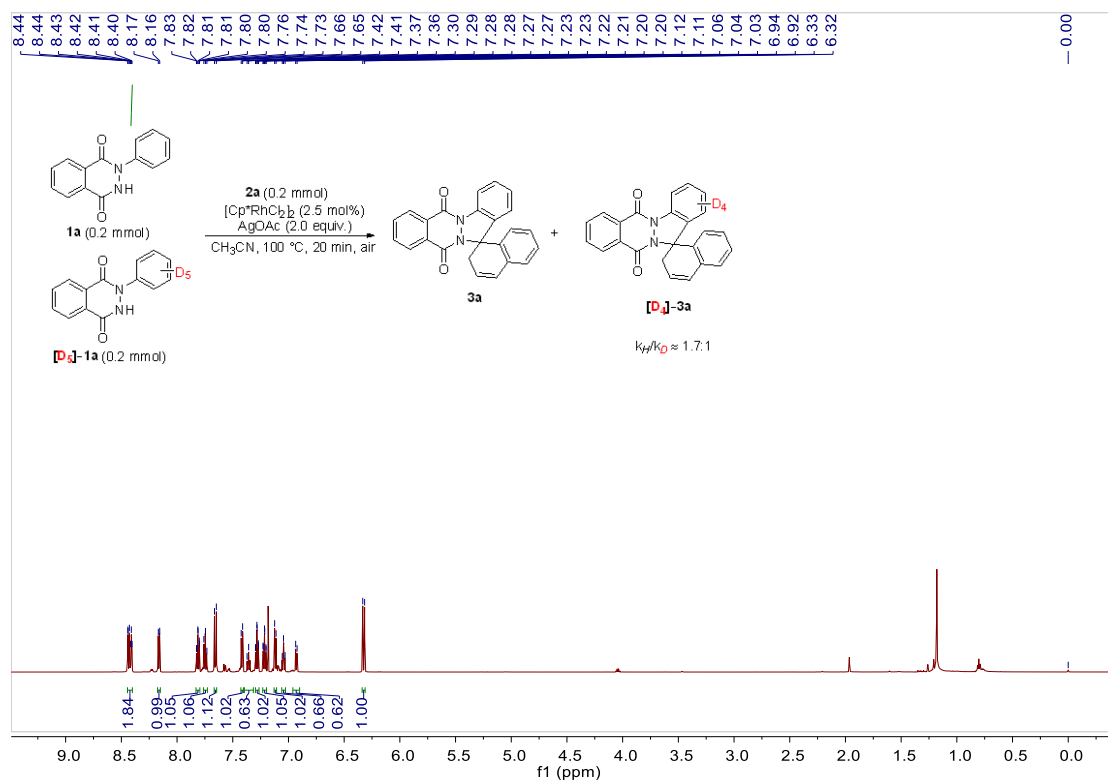
Compound **1c** (50.5 mg, 0.20 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (3.1 mg, 0.005 mmol), AgOAc (66.8 mg, 0.40 mmol) and  $\text{CD}_3\text{OD}$  (72.1 mg, 2.00 mmol) were dissolved in  $\text{CH}_3\text{CN}$  (2.0 mL). The mixture was stirred at 100 °C under air for 12 hours. The resulting mixture was cooled to room temperature and then diluted with dichloromethane (20 mL). The suspension was then transferred to a round bottom flask (50 mL), concentrated under reduced pressure. The residue was purified by flash chromatography (56% recovered). The deuterated ratio was calculated from  $^1\text{H}$  NMR analysis. (~69% D-incorporation was observed).



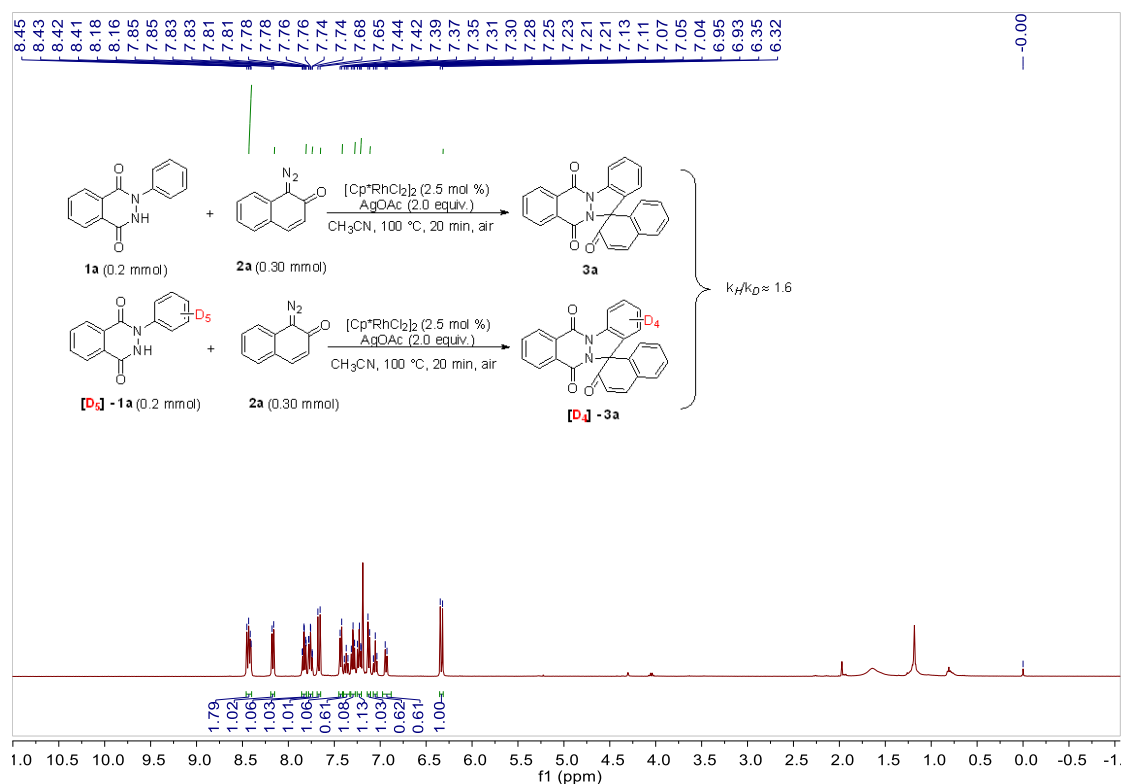
### 3.2 Kinetic isotope effect



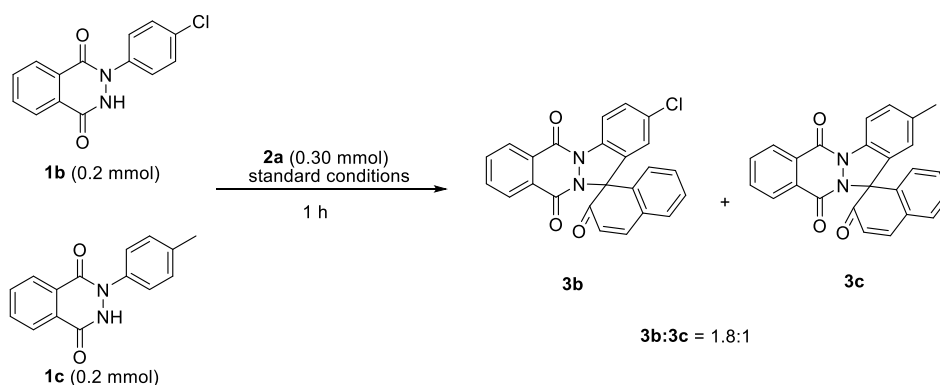
2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol) and **[D<sub>5</sub>]-2-phenyl-2,3-dihydrophthalazine-1,4-dione [D<sub>5</sub>]-1a** (33.4 mg, 0.20 mmol), 1-diazonaphthalen-2(1*H*)-one **2a** (34.0 mg, 0.20 mmol), **[Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub>** (3.1 mg, 0.005 mmol) and **AgOAc** (66.8 mg, 0.40 mmol), were dissolved in **CH<sub>3</sub>CN** (2.0 mL). The mixture was stirred at 100 °C under air for 20 minutes. The resulting mixture was cooled to room temperature and then diluted with dichloromethane (20 mL). The suspension was then transferred to a round bottom flask (50 mL), concentrated under reduced pressure. Purification was performed by flash column chromatography on silica gel using **EtOAc** and petroleum ether to afford the desired products. KIE value ( $k_H/k_D \approx 1.7$ ) was determined on the basis of <sup>1</sup>H NMR analysis.



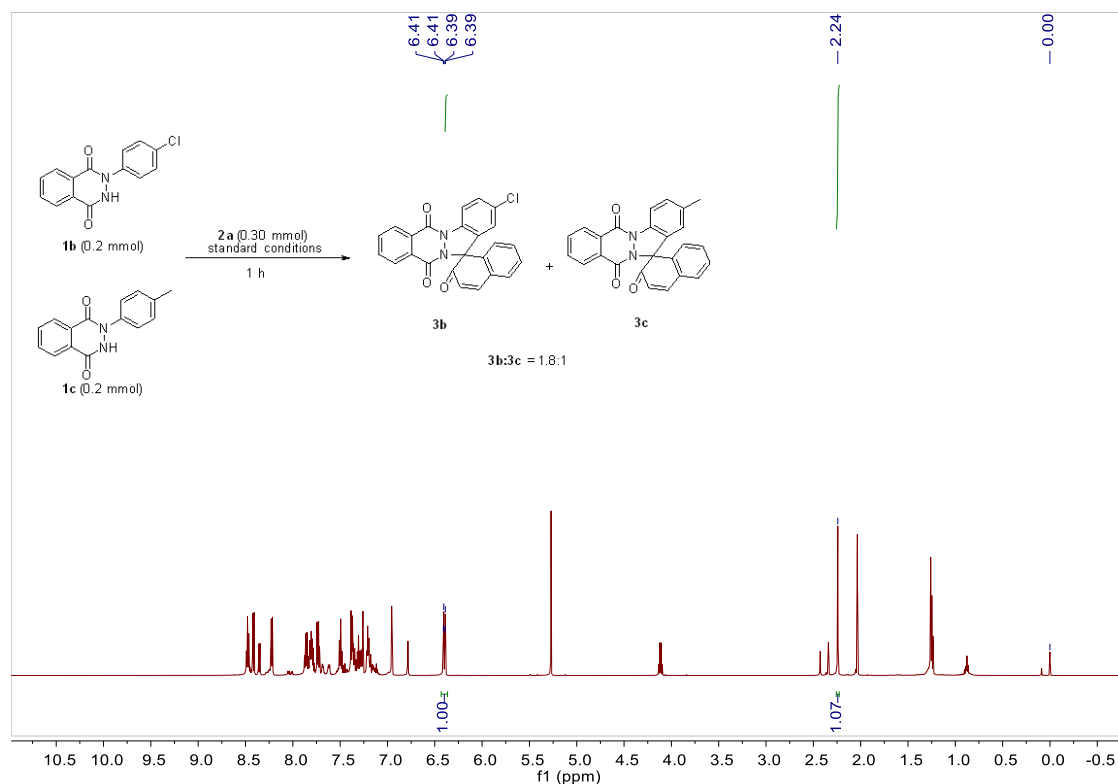
2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol) and **[D<sub>5</sub>]-1a** (33.4 mg, 0.2 mmol), 1-diazonaphthalen-2(1*H*)-one **2a** (51.0 mg, 0.30 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (3.1 mg, 0.005 mmol) and AgOAc (66.8 mg, 0.40 mmol), were dissolved in  $\text{CH}_3\text{CN}$  (2.0 mL). These two reaction mixtures were stirred side-by-side in the same oil bath at 100 °C for 20 minutes. The reactions tubes were quenched at 0 °C and these two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using PE/EA to afford the mixed product. KIE value ( $k_H/k_D \approx 1.6$ ) was determined on the basis of <sup>1</sup>H NMR analysis.



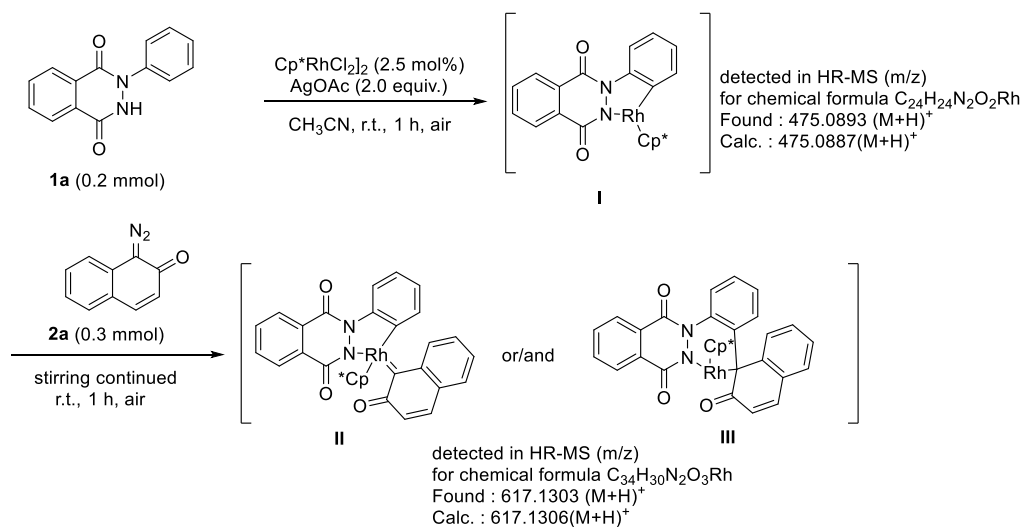
#### 4. Competition experiments



To an oven-dried 10 mL pressure tube was added **1b** (54.5 mg, 0.20 mmol), **1c** (50.4mg, 0.20 mmol), 1-diazonaphthelen-2(1*H*)-one **2a** (51.0 mg, 0.30 mmol), [Cp\*RhCl<sub>2</sub>]<sub>2</sub> (3.1 mg, 0.005 mmol), AgOAc (66.8 mg, 0.40 mmol), and CH<sub>3</sub>CN (2.0 mL) under air. The mixture was stirred for 1 h at 100 °C before diluted with dichloromethane (20 mL), The suspension was then transferred to a round bottom flask (50 mL), concentrated under reduced pressure. Purification was performed by flash column chromatography on silica gel using EtOAc and petroleum ether to afford the desired products, **3b** and **3c** with a ratio of 1.8:1 was determined on the basis of <sup>1</sup>H NMR analysis.

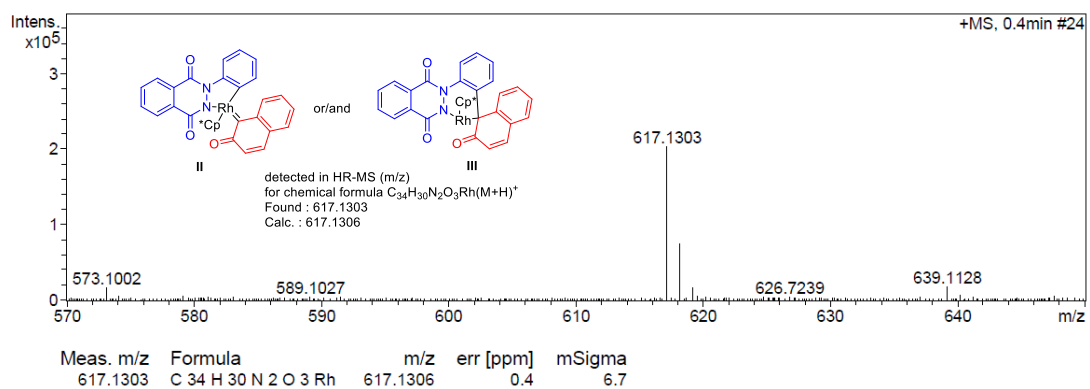
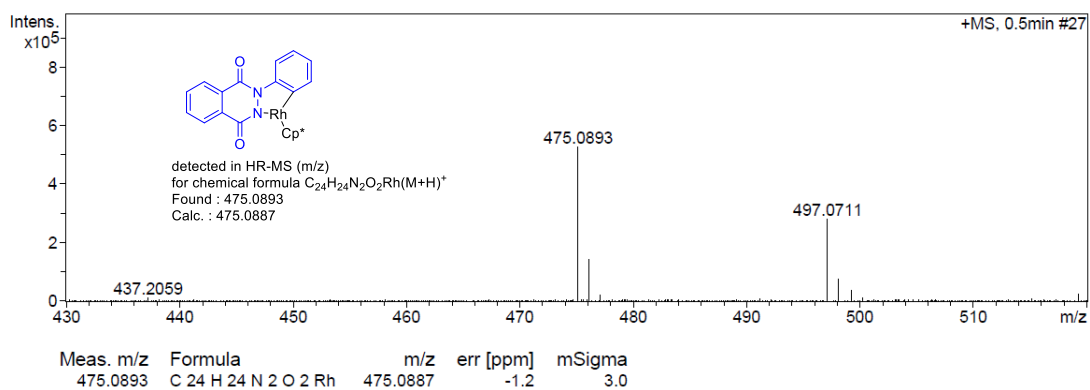


## 5. Intermediate capture experiments



To an oven-dried 10 mL pressure tube was added 2-phenyl-2,3-dihydrophthalazine-1,4-dione **1a** (47.6 mg, 0.20 mmol),  $[\text{Cp}^*\text{RhCl}_2]_2$  (3.1 mg, 0.005 mmol), AgOAc (66.8 mg, 0.40 mmol), and  $\text{CH}_3\text{CN}$  (2.0 mL) under air. The mixture was stirred for 1 hour at room temperature, and the reaction mixture characterized by HRMS. To the reaction mixture was added 1-diazonaphthelen-2(1*H*)-one **2a** (51.1 mg, 0.30 mmol), further stirring the reaction mixture for another 1 hour at room temperature, and the reaction mixture characterized by HRMS.





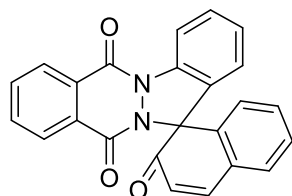
## 6. References

- [1] S. Rajkumar, S. Antony Savarimuthu, R. Senthil Kumaran, C. M. Nagaraja, T. Gandhi, *Chem. Commun.* **2016**, 52, 2509-2512.
- [2] X. Han, L. Kong, J. Feng, X. Li, *Chem. Commun.* **2020**, 56, 5528-5531;
- [3] B. Ma, P. Wu, X. Wang, Z. Wang, H.-X. Lin, H.-X. Dai, *Angew. Chem., Int. Ed.* **2019**, 58, 13335-13339.

## 7. Analytical data and copies of NMR spectra

### 7.1 Analytical data for products.

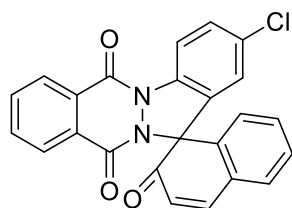
#### 2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (**3a**)



**3a**

Product **3a** was isolated as a light yellow solid (68.9 mg, 91%); m.p. 292-293 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.53-8.50 (m, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.26-8.21 (m, 1H), 7.89 (td, *J* = 7.2, 1.2 Hz, 1H), 7.82 (td, *J* = 7.8, 1.2 Hz, 1H), 7.73 (d, *J* = 10.2 Hz, 1H), 7.52-7.47 (m, 1H), 7.46-7.41 (m, 1H), 7.36 (td, *J* = 7.8, 1.2 Hz, 1H), 7.29 (td, *J* = 7.8, 1.2 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 (td, *J* = 7.2, 1.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 10.2 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 192.0, 154.6, 146.6, 140.3, 136.00, 133.7, 133.6, 131.2, 130.2, 130.2, 128.9, 128.8, 128.7, 128.4, 127.8, 127.8, 126.3, 126.04, 123.8, 121.6, 116.8, 75.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>24</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 379.1077, found: 379.1066.

#### 2-Chloro-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (**3b**)

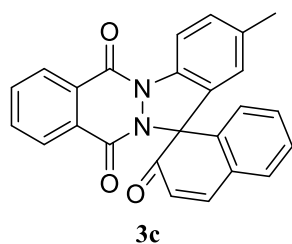


**3b**

Product **3b** was isolated as a light yellow solid (76.8 mg, 93%); m.p. 256-257 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51-8.46 (m, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.26-8.20 (m, 1H), 7.90 (td, *J* = 7.6, 1.4 Hz, 1H), 7.84 (td, *J* = 7.6, 1.4 Hz, 1H), 7.76 (d, *J* = 10.0 Hz, 1H), 7.55-7.49 (m, 1H), 7.44-7.37 (m, 2H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (d, *J* =

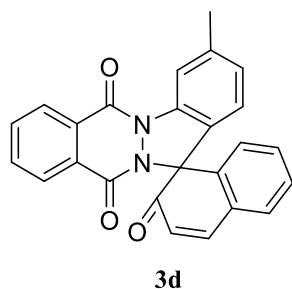
7.6 Hz, 1H), 6.96 (d,  $J = 2.0$  Hz, 1H), 6.41 (d,  $J = 10.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5, 154.5, 146.9, 139.5, 134.5, 133.9, 133.8, 131.4, 131.3, 130.4, 129.9, 129.8, 129.3, 128.7, 128.6, 127.8, 126.1, 123.6, 121.9, 117.7, 74.8. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{24}\text{H}_{14}\text{ClN}_2\text{O}_3^+$ : 413.0687, found: 413.0687.

**2-Methyl-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**  
**(3c)**



Product **3c** was isolated as a light yellow solid (69.8 mg, 89%); m.p. 259-261 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J = 7.6$  Hz, 1H), 8.35 (d,  $J = 8.4$  Hz, 1H), 8.23 (d,  $J = 7.2$  Hz, 1H), 7.88 (t,  $J = 7.4$  Hz, 1H), 7.81 (t,  $J = 7.2$  Hz, 1H), 7.73 (d,  $J = 10.0$  Hz, 1H), 7.50 (d,  $J = 7.4$  Hz, 1H), 7.36 (t,  $J = 7.2$  Hz, 1H), 7.29 (t,  $J = 7.4$  Hz, 1H), 7.23 (d,  $J = 8.2$  Hz, 1H), 7.18 (d,  $J = 7.6$  Hz, 1H), 6.78 (s, 1H), 6.40 (d,  $J = 10.0$  Hz, 1H), 2.25 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 154.5, 154.2, 146.6, 140.4, 136.55, 133.8, 133.7, 133.4, 131.12, 130.8, 130.3, 130.2, 128.9, 128.8, 128.7, 128.6, 127.7, 126.0, 123.9, 121.9, 116.5, 75.2, 21.1. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{25}\text{H}_{17}\text{N}_2\text{O}_3^+$ : 393.1234, found: 393.1229.

**3-Methyl-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**  
**(3d)**

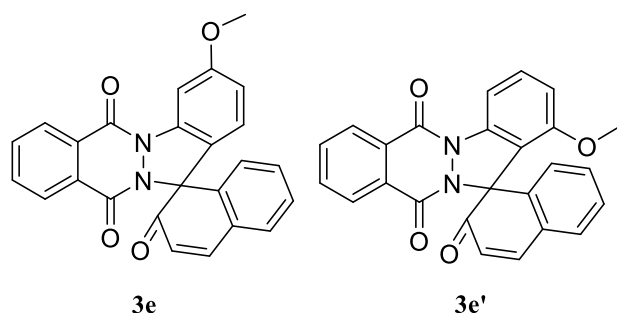


Product **3d** was isolated as a light yellow solid (70.6 mg, 90%); m.p. 220-221 °C;  $^1\text{H}$

NMR (400 MHz, CDCl<sub>3</sub>) δ 8.55-8.47 (m, 1H), 8.34 (s, 1H), 8.26-8.20 (m, 1H), 7.92-7.86 (m, 1H), 7.85-7.79 (m, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.51-7.45 (m, 1H), 7.39-7.32 (m, 1H), 7.31-7.27 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.2, 154.5, 154.5, 146.6, 140.8, 140.5, 136.1, 133.7, 133.5, 131.1, 130.2, 130.1, 128.8, 128.7, 127.8, 127.7, 127.1, 125.9, 125.8, 123.9, 121.2, 117.2, 75.1, 21.7. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>25</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 393.1234, found: 393.1236.

**3-Methoxy-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (3e)**

**1-Methoxy-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (3e')**



Product **3e** and **3e'** was isolated as a light yellow solid (72.7 mg, 89%, 3e:3e' = 3.35:1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.52-8.48 (m, 0.77H), 8.48-8.45 (m, 0.23H), 8.25-8.22 (m, 0.77H), 8.18-8.16 (m, 0.23H), 8.12-8.06 (m, 1H), 7.91-7.76 (m, 2H), 7.70 (d, *J* = 10.2 Hz, 0.79H), 7.64 (d, *J* = 10.2 Hz, 0.25H), 7.49-7.33 (m, 2H), 7.33-7.27 (m, 1H), 7.25-7.22 (m, 0.23H), 7.21-7.17 (d, 0.77H), 7.12 (d, *J* = 7.8 Hz, 0.23H), 6.87 (d, *J* = 8.4 Hz, 0.77H), 6.68-6.63 (m, 1H), 6.48 (d, *J* = 10.2 Hz, 0.23H), 6.38 (d, *J* = 10.2 Hz, 0.77H), 3.86 (s, 2.31H), 3.57 (s, 0.69H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 193.2, 192.3, 161.2, 154.7, 154.5, 153.9, 153.6, 146.5, 144.8, 140.7, 138.9, 137.9, 137.3, 137.0, 133.7, 133.6, 133.6, 133.5, 131.8, 131.1, 130.8, 130.7, 130.3, 130.1, 129.1, 128.8, 128.8, 128.7, 128.7, 128.6, 127.8, 127.8, 127.7, 127.7, 126.7, 126.0, 125.1, 123.9, 122.2, 120.5, 119.3, 113.5, 109.0, 108.6, 101.8, 75.0, 72.2, 55.8,

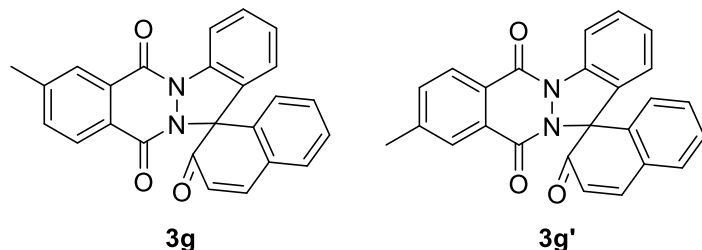
55.6. HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{22}H_{25}N_2O_3^+$ : 365.1860, found: 365.1865.

**8-Methyl-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**

**(3g)**

**9-Methyl-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**

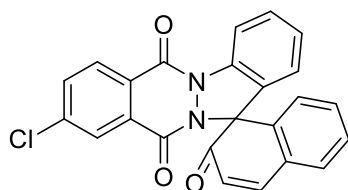
**(3g')**



Product **3g** and **3g'** was isolated as a light yellow solid (70.6 mg, 90%, 3g:3g' = 1:1.33);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.51-8.45 (m, 1H), 8.39 (d,  $J = 8.0$  Hz, 0.43H), 8.30 (s, 0.57H), 8.12 (d,  $J = 8.0$  Hz, 0.57H), 8.03 (s, 0.43H), 7.74 (d,  $J = 10.0$  Hz, 1H), 7.70 (d,  $J = 8.0$  Hz, 0.43H), 7.63 (d,  $J = 8.0$  Hz, 0.57H), 7.51 (s, 0.43H), 7.49 (s, 0.57H), 7.46-7.40 (m, 1H), 7.39-7.33 (m, 1H), 7.32-7.27 (m, 1H), 7.20 (d,  $J = 3.2$  Hz, 0.57H), 7.18 (d,  $J = 3.2$  Hz, 0.43H), 7.14-7.08 (m, 1H), 7.01 (s, 0.57H), 7.00 (s, 0.43H), 6.40 (d,  $J = 10.0$  Hz, 1H), 2.59 (s, 1.71H), 2.52 (s, 1.29H).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  192.2, 192.1, 154.7, 154.7, 154.7, 154.6, 146.7, 145.0, 144.8, 140.4, 140.3, 136.0, 134.8, 134.7, 131.2, 130.2, 130.1, 130.1, 130.0, 128.9, 128.7, 128.5, 128.4, 128.2, 127.8, 127.8, 127.8, 127.6, 126.2, 126.1, 126.0, 125.9, 123.8, 121.6, 116.8, 116.7, 75.2, 75.1, 21.9, 21.8. HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{25}H_{17}N_2O_3^+$ : 393.1234, found: 393.1246.

**9-Chloro-2'H-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**

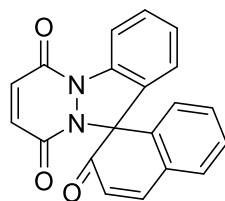
**(3h)**



**3h**

Product **3h** was isolated as a light yellow solid (53.6 mg, 65%); m.p. 243-244 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52-8.40 (m, 2H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.79-7.71 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.33-7.28 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.9, 153.9, 153.3, 146.8, 140.8, 139.9, 135.7, 133.9, 131.5, 131.2, 130.3, 130.3, 129.5, 129.0, 128.7, 128.3, 127.6, 127.0, 126.6, 126.0, 123.7, 121.7, 116.9, 75.4. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>24</sub>H<sub>13</sub>ClN<sub>2</sub>NaO<sub>3</sub><sup>+</sup>: 435.0507, found: 435.0524.

**2H-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione (3i)**

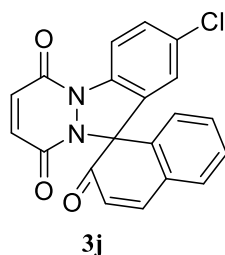


**3i**

Product **3i** was isolated as a yellow solid (47.3 mg, 72%); m.p. 254-256 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.51-7.45 (m, 1H), 7.44-7.35 (m, 2H), 7.34-7.29 (m, 1H), 7.16-7.08 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 10.4 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.1, 153.5, 153.4, 146.9, 139.0, 136.4, 135.4, 134.4, 131.1, 130.4, 130.2, 129.0, 128.8, 128.0, 126.7, 125.6, 123.7, 121.6, 116.4, 75.7. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>20</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 329.0921, found: 329.0914.

**2'-Chloro-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

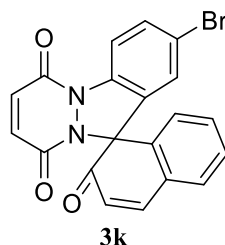
**(3j)**



Product **3j** was isolated as a yellow solid (55.9 mg, 77%); m.p. 256-257 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 10.0 Hz, 1H), 7.54-7.49 (d, *J* = 7.4 Hz, 1H), 7.45-7.31 (m, 3H), 7.17-7.08 (m, 2H), 7.01-6.92 (m, 2H), 6.38 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.57, 153.42, 153.31, 147.12, 138.31, 136.2, 134.6, 134.0, 132.0, 131.3, 130.6, 130.4, 129.4, 129.4, 128.7, 125.7, 123.6, 121.9, 117.4, 75.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>20</sub>H<sub>12</sub>ClN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 363.0531, found: 363.0529.

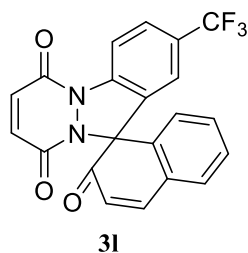
**2'-Bromo-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

**(3k)**



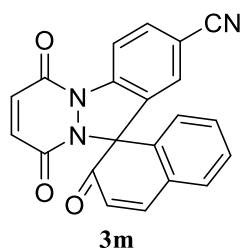
Product **3k** was isolated as a yellow solid (64.3 mg, 79%); m.p. 263-264 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 10.0 Hz, 1H), 7.57-7.49 (m, 2H), 7.54-7.39 (m, 1H), 7.38-7.32 (m, 1H), 7.17-7.06 (m, 3H), 6.97 (d, *J* = 10.2 Hz, 1H), 6.38 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.58, 153.49, 153.29, 147.1, 138.3, 136.2, 134.7, 134.5, 133.3, 131.4, 130.6, 129.7, 129.4, 128.7, 125.7, 124.8, 123.6, 119.4, 117.7, 75.2. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>20</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 407.0026, found: 407.0017.

**2'-(Trifluoromethyl)-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione (3l)**



Product **3l** was isolated as a yellow solid (57.1 mg, 72%); m.p. 246-248 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.47 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 10.0 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.46-7.41 (m, 1H), 7.40-7.33 (m, 1H), 7.18 (s, 1H), 7.17-7.11 (m, 2H), 7.01 (d, *J* = 10.4 Hz, 1H), 6.40 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.6, 153.8, 153.3, 147.4, 138.2, 137.9, 136.1, 135.1, 131.5, 130.8, 129.6, 128.9, 128.7, 128.6, 128.0 (q, *J* = 3.6 Hz), 125.8, 123.5, 119.0 (q, *J* = 3.6 Hz), 116.5, 75.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.00. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>21</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 397.0795, found: 397.0796.

**2,6',9'-Trioxo-6',9'-dihydro-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2'-carbonitrile (3m)**

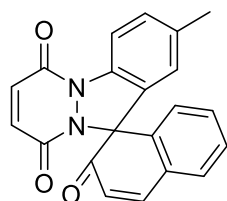


Product **3m** was isolated as a yellow solid (63.6 mg, 90%); m.p. 270-271 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 10.0 Hz, 1H), 7.71 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.56-7.51 (m, 1H), 7.47-7.41 (m, 1H), 7.40-7.33 (m, 1H), 7.25-7.21 (m, 1H), 7.17-7.08 (m, 2H), 7.00 (d, *J* = 10.4 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.2, 153.9, 153.3, 147.3, 138.3, 138.0, 135.9, 135.3, 134.7, 131.5, 130.8, 129.7, 128.9, 128.7, 125.8, 125.7, 123.3, 117.4, 116.7, 110.0, 75.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>21</sub>H<sub>12</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>: 354.0873, found: 354.0879.



**2'-Methyl-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

**(3n)**

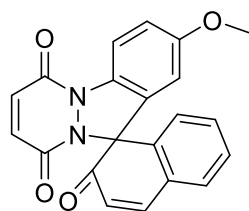


**3n**

Product **3n** was isolated as a yellow solid (45.9 mg, 67%); m.p. 259-260 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.41-7.36 (m, 1H), 7.35-7.30 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.15-7.07 (m, 2H), 6.94 (d, *J* = 10.2 Hz, 1H), 6.78 (s, 1H), 6.38 (d, *J* = 10.0 Hz, 1H), 2.25 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.2, 153.4, 153.2, 146.8, 139.1, 137.1, 136.4, 134.1, 133.2, 131.1, 130.8, 130.3, 129.0, 128.8, 128.1, 125.6, 123.8, 121.8, 116.2, 75.6, 21.2. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 343.1077, found: 343.1071.

**2'-Methoxy-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

**(3o)**



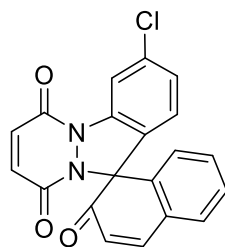
**3o**

Product **3o** was isolated as a yellow solid (58.1 mg, 81%); m.p. 232-234 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 10.0 Hz, 1H), 7.48 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.15-7.07 (m, 2H), 6.95-6.92 (m, 1H), 6.91-6.87 (m, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 10.0 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.0, 158.4, 153.5, 152.9, 146.8, 139.0, 136.5, 133.8, 131.2, 130.4, 129.6, 129.1, 129.10, 128.83, 125.7, 123.9, 117.6, 114.8, 107.8, 75.6, 55.8. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>:

C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup>: 359.1026, found: 359.1030.

**3'-Chloro-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

**(3p)**

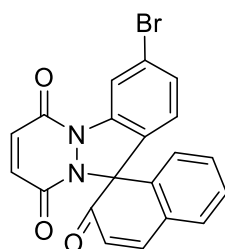


**3p**

Product **3p** was isolated as a yellow solid (60.9 mg, 84%); m.p. 283-284 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43-7.37 (m, 1H), 7.37-7.31 (m, 1H), 7.16-7.08 (m, 3H), 6.98 (d, *J* = 10.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.36 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.8, 153.6, 153.3, 147.0, 138.5, 136.2, 136.2, 136.1, 134.8, 131.3, 130.5, 129.3, 128.7, 126.9, 126.4, 125.7, 123.6, 122.5, 116.6, 75.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>20</sub>H<sub>12</sub>ClN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 363.0531, found: 363.0536.

**3'-Bromo-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione**

**(3q)**



**3q**

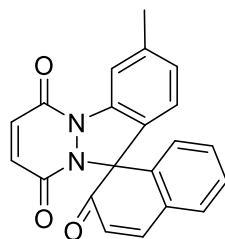
Product **3q** was isolated as a yellow solid (52.1 mg, 64%); m.p. 296-297 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.55 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 10.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.43-7.37 (m, 1H), 7.37-7.31 (m, 1H), 7.29-7.23 (m, 1H), 7.16-7.09 (m, 2H), 6.98 (d, *J* = 10.2 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.36 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 190.7, 153.6, 153.3, 147.0, 138.5, 136.3, 136.1, 134.8,

131.3, 130.5, 129.8, 129.3, 128.7, 127.0, 125.7, 123.9, 123.6, 122.8, 119.35, 75.39.

HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{20}H_{12}BrN_2O_3^+$ : 407.0026, found: 407.0021.

### 3'-Methyl-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione

(3r)

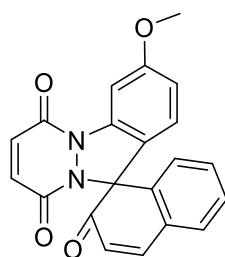


3r

Product **3r** was isolated as a yellow solid (55.5 mg, 81%); m.p. 252-254 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.20 (s, 1H), 7.68 (d,  $J = 10.2$  Hz, 1H), 7.51-7.44 (m, 1H), 7.36 (td,  $J = 7.2, 1.2$  Hz, 1H), 7.31 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.11 (s, 1H), 7.10-7.08 (m, 1H), 6.96-6.94 (m, 1H), 6.94-6.92 (m, 1H), 6.86 (d,  $J = 7.8$  Hz, 1H), 6.35 (d,  $J = 9.6$  Hz, 1H), 2.39 (s, 3H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  191.2, 153.6, 153.5, 146.7, 140.9, 139.3, 136.4, 135.7, 134.3, 131.1, 130.3, 129.0, 128.9, 127.6, 125.61, 125.49, 123.9, 121.2, 116.8, 75.6, 21.6. HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{21}H_{15}N_2O_3^+$ : 343.1077, found: 343.1080.

### 3'-Methoxy-2*H*-spiro[naphthalene-1,11'-pyridazino[1,2-*a*]indazole]-2,6',9'-trione

(3s)

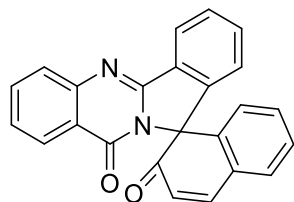


3s

Product **3s** was isolated as a yellow solid (51.6 mg, 72%); m.p. 252-253 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.96 (d,  $J = 2.4$  Hz, 1H), 7.67 (d,  $J = 9.6$  Hz, 1H), 7.46 (d,  $J = 7.8$  Hz, 1H), 7.35 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.31 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.12 (d,  $J = 7.8$  Hz, 1H), 7.09 (d,  $J = 10.2$  Hz, 1H), 6.94 (d,  $J = 10.2$  Hz, 1H), 6.86 (d,  $J = 8.4$  Hz,

1H), 6.66 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.35 (d,  $J = 9.6$  Hz, 1H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 161.2, 153.7, 153.4, 146.6, 139.4, 136.8, 136.3, 134.5, 131.1, 130.3, 128.9, 128.8, 125.6, 123.9, 122.1, 120.1, 113.7, 101.5, 75.4, 55.9. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_4^+$ : 359.1026, found: 359.1029.

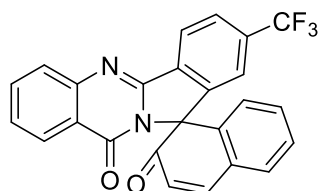
**2'H,10H-spiro[isoindolo[1,2-b]quinazoline-12,1'-naphthalene]-2',10-dione (3u)**



**3u**

Product **3u** was isolated as a light yellow solid (37.7 mg, 52%); m.p. 258-259 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27-8.20 (m, 2H), 7.92 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.83-7.76 (m, 2H), 7.54 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.51 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.48-7.42 (m, 2H), 7.34 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.22-7.15 (m, 2H), 6.78 (d,  $J = 7.8$  Hz, 1H), 6.48 (d,  $J = 10.2$  Hz, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2, 158.9, 155.5, 149.4, 146.8, 144.2, 138.0, 134.6, 132.9, 131.3, 131.0, 130.4, 129.8, 129.5, 128.9, 127.6, 126.9, 126.7, 125.1, 125.0, 124.6, 121.7, 121.7, 74.78. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{24}\text{H}_{15}\text{N}_2\text{O}_2^+$ : 363.1128, found: 363.1138.

**2-(Trifluoromethyl)-2'H,10H-spiro[isoindolo[1,2-b]quinazoline-12,1'-naphthalene]-2',10-dione (3v)**

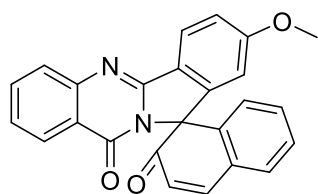


**3v**

Product **3v** was isolated as a light yellow solid (38.7mg, 45%); m.p. 267-268 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (d,  $J = 8.0$  Hz, 1H), 8.24 (dd,  $J = 8.0, 1.6$  Hz, 1H), 7.94 (d,  $J = 8.2$  Hz, 1H), 7.89-7.79 (m, 3H), 7.57 (d,  $J = 7.6$  Hz, 1H), 7.52 (t,  $J = 7.6$

Hz, 1H), 7.41 (t,  $J = 7.5$  Hz, 1H), 7.37 (s, 1H), 7.28-7.22 (m, 1H), 6.79 (d,  $J = 7.8$  Hz, 1H), 6.52 (d,  $J = 10.0$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  190.7, 158.6, 153.9, 149.1, 147.4, 144.4, 136.9, 134.9, 134.9, 134.7, 134.4, 131.3, 130.8, 129.4, 127.9, 127.4, 127.1, 127.1, 127.0, 125.2, 125.1, 124.8, 121.9, 119.0 (q,  $J = 4.0$  Hz), 74.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  62.5. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{25}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2^+$ : 431.1002, found: 431.1013.

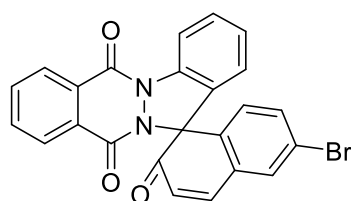
**2-Methoxy-2'H,10H-spiro[isoindolo[1,2-b]quinazoline-12,1'-naphthalene]-2',10-dione (3w)**



**3w**

Product **3w** was isolated as a light yellow solid (31.4 mg, 40%); m.p. 287-288 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23-8.13 (m, 2H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.83-7.76 (m, 2H), 7.52 (d,  $J = 7.6$  Hz, 1H), 7.44 (t,  $J = 7.6$  Hz, 1H), 7.36 (t,  $J = 7.6$  Hz, 1H), 7.23 (t,  $J = 7.6$  Hz, 1H), 7.07 (dd,  $J = 8.6, 2.0$  Hz, 1H), 6.81 (d,  $J = 7.8$  Hz, 1H), 6.62 (d,  $J = 2.0$  Hz, 1H), 6.49 (d,  $J = 10.0$  Hz, 1H), 3.78 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2, 163.6, 158.8, 155.3, 149.5, 146.8, 146.2, 138.0, 134.6, 131.1, 130.5, 129.3, 128.9, 127.2, 126.9, 126.3, 126.0, 125.1, 124.9, 123.4, 121.2, 116.2, 106.8, 74.3, 55.8. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{25}\text{H}_{17}\text{N}_2\text{O}_3^+$ : 393.1234, found: 393.1241.

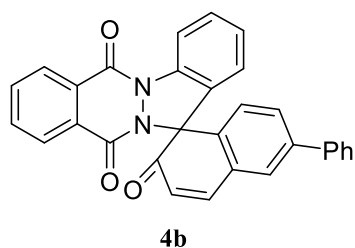
**6'-Bromo-2'H-spiro[indazolo[1,2-b]phthalazine-13,1'-naphthalene]-2',6,11-trione (4a)**



**4a**

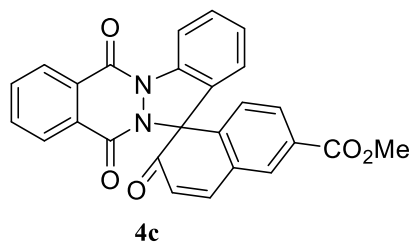
Product **4a** was isolated as a light yellow solid (80.5 mg, 88%); m.p. 264-265 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.50 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.90 (td, *J* = 7.8, 1.2 Hz, 1H), 7.83 (td, *J* = 7.8, 1.2 Hz, 1H), 7.67-7.63 (m, 2H), 7.47-7.43 (m, 1H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.14 (td, *J* = 7.8, 1.2 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 10.2 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 191.4, 154.7, 154.5, 144.9, 139.0, 136.0, 133.9, 133.7, 132.7, 130.6, 130.5, 130.2, 128.5, 127.9, 127.8, 127.76, 126.35, 125.05, 122.9, 121.6, 116.9, 74.9. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>24</sub>H<sub>14</sub>BrN<sub>2</sub>O<sub>3</sub><sup>+</sup>: 457.0182, found: 457.0190.

**6'-Phenyl-2'*H*-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione**  
**(4b)**



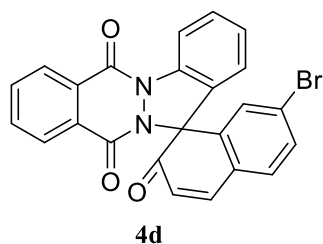
Product **4b** was isolated as a light yellow solid (54.5 mg, 60%); m.p. 234-235 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56-8.48 (m, 2H), 8.29-8.23 (m, 1H), 7.91 (td, *J* = 7.6, 1.2 Hz, 1H), 7.87-7.77 (m, 2H), 7.69 (d, *J* = 1.8 Hz, 1H), 7.58-7.52 (m, 2H), 7.52-7.42 (m, 4H), 7.41-7.35 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.19-7.12 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.46 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.1, 154.7, 154.6, 146.6, 142.1, 139.4, 138.9, 136.0, 133.8, 133.6, 130.3, 130.2, 129.8, 129.2, 128.9, 128.9, 128.7, 128.4, 128.0, 127.9, 127.8, 127.0, 126.58, 126.3, 124.2, 121.7, 116.9, 75.1. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>30</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 455.1390, found: 455.1405.

**Methyl 2',6,11-trioxo-6,11-dihydro-2'H-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-6'-carboxylate (4c)**



Product **4c** was isolated as a light yellow solid (62.0 mg, 71%); m.p. 267-268 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54-8.47 (m, 2H), 8.22 (d, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 7.95 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.89 (td, *J* = 7.6, 1.6 Hz, 1H), 7.85-7.77 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 10.0 Hz, 1H), 3.91 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.3, 165.6, 154.7, 154.5, 145.7, 144.4, 136.0, 133.9, 133.7, 131.9, 131.2, 130.8, 130.5, 130.1, 129.0, 128.4, 127.9, 127.8, 127.4, 126.4, 126.2, 124.6, 121.5, 116.9, 75.2, 52.5. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>26</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub><sup>+</sup>: 437.1132, found: 437.1139.

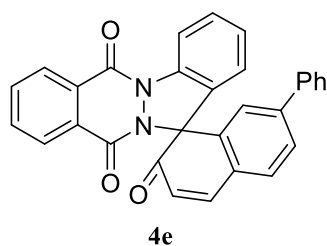
**7'-Bromo-2'H-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (4d)**



Product **4d** was isolated as a light yellow solid (71.3 mg, 78%); m.p. 265-266 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.53-8.51 (m, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.26-8.22 (m, 1H), 7.91 (td, *J* = 7.8, 1.2 Hz, 1H), 7.85 (td, *J* = 7.8, 1.2 Hz, 1H), 7.67 (d, *J* = 10.2 Hz, 1H), 7.50 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.48-7.44 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.14 (td, *J* = 7.2, 1.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 9.6 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 191.2, 154.9, 154.6, 145.4, 142.0, 136.0, 134.0, 133.7, 132.3, 131.3, 130.5, 130.2, 129.3, 128.5, 128.0, 127.9, 127.78,

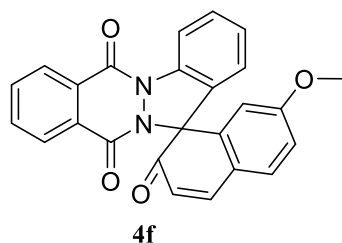
127.7, 126.4, 126.0, 124.2, 121.6, 117.0, 74.8. HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{24}H_{14}BrN_2O_3^+$ : 457.0182, found: 457.0198.

**7'-Phenyl-2'H-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (4e)**



Product **4e** was isolated as a light yellow solid (84.5mg, 93%); m.p. 153-155 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.55-8.47 (m, 1H), 8.24 (dd,  $J = 7.8, 1.2$  Hz, 2H), 7.89 (td,  $J = 7.2, 1.2$  Hz, 1H), 7.82 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.77 (d,  $J = 9.6$  Hz, 1H), 7.60-7.55 (m, 2H), 7.46-7.42 (m, 1H), 7.39-7.35 (m, 3H), 7.34-7.30 (m, 2H), 7.30 -7.26 (m, 1H), 7.13 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.04 (dd,  $J = 7.8, 1.2$  Hz, 1H), 6.41 (d,  $J = 10.2$  Hz, 1H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  192.0, 154.8, 154.6, 146.3, 144.1, 140.9, 139.3, 136.0, 133.8, 133.6, 130.7, 130.2, 128.8, 128.7, 128.5, 128.2, 127.8, 127.6, 127.1, 126.3, 124.7, 123.6, 121.7, 116.8, 75.4. HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{30}H_{19}N_2O_3^+$ : 455.1390, found: 455.1399.

**7'-Methoxy-2'H-spiro[indazolo[1,2-*b*]phthalazine-13,1'-naphthalene]-2',6,11-trione (4f)**

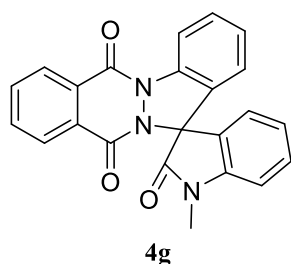


Product **4f** was isolated as a light yellow solid (72.7mg, 89%); m.p. 306-307 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.52-8.49 (m, 1H), 8.47 (d,  $J = 8.4$  Hz, 1H), 8.25 (d,  $J = 7.8$  Hz, 1H), 7.89 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.82 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.68 (d,  $J =$



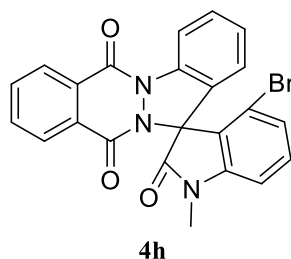
10.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.12 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.02 (d,  $J = 7.8$  Hz, 1H), 6.85 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.71 (d,  $J = 2.4$  Hz, 1H), 6.25 (d,  $J = 10.2$  Hz, 1H), 3.68 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9, 162.0, 154.6, 154.5, 146.7, 142.6, 135.9, 133.7, 133.6, 132.0, 130.2, 130.1, 128.7, 128.5, 127.8, 126.2, 122.0, 121.6, 121.0, 116.8, 113.2, 112.9, 75.4, 55.4. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{H}]^+$ :  $\text{C}_{25}\text{H}_{17}\text{N}_2\text{O}_4^+$ : 409.1183, found: 409.1183.

#### 1'-Methylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4g)



Product **4g** was isolated as a light yellow solid (42.0 mg, 55%); m.p. 294-296 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52-8.42 (m, 2H), 8.20 (d,  $J = 7.6$  Hz, 1H), 7.85 (t,  $J = 7.4$  Hz, 1H), 7.79 (t,  $J = 7.4$  Hz, 1H), 7.49 (t,  $J = 7.8$  Hz, 1H), 7.41 (td,  $J = 7.4, 1.6$  Hz, 1H), 7.20 (t,  $J = 7.6$  Hz, 1H), 7.10-7.00 (m, 3H), 6.93 (d,  $J = 7.6$  Hz, 1H), 3.41 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 154.5, 154.4, 143.9, 136.8, 133.7, 133.5, 130.6, 130.4, 129.9, 128.3, 127.7, 127.5, 126.6, 126.5, 126.3, 123.6, 123.6, 122.07, 116.13, 108.9, 72.1, 27.1. HRMS (ESI)  $m/z$  calcd for  $[\text{M}+\text{Na}]^+$ :  $\text{C}_{23}\text{H}_{15}\text{N}_3\text{NaO}_3^+$ : 404.1006, found: 404.1016.

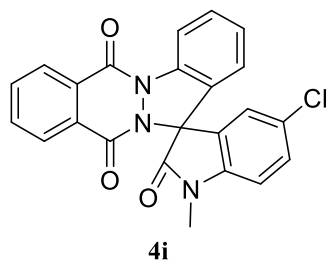
#### 4'-Bromo-1'-methylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4h)



Product **4h** was isolated as a light yellow solid (41.4 mg, 45%); m.p. 304-306 °C;  $^1\text{H}$

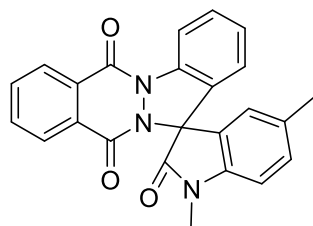
NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51-8.46 (m, 2H), 8.23-8.19 (m, 1H), 7.88 (td, *J* = 7.8, 1.2 Hz, 1H), 7.81 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55-7.51 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.4, 0.6 Hz, 1H), 6.99 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.41 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.5, 154.7, 154.2, 145.7, 138.3, 133.8, 133.6, 131.8, 130.7, 130.1, 127.9, 127.9, 127.6, 127.2, 126.4, 124.8, 123.7, 121.6, 118.9, 116.0, 107.9, 72.8, 27.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>23</sub>H<sub>15</sub>BrN<sub>3</sub>O<sub>3</sub><sup>+</sup>: 460.0291, found: 460.0298.

**5'-Chloro-1'-methylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4i)**



Product **4i** was isolated as a light yellow solid (30.8 mg, 37%); m.p. 328-330 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51-8.45 (m, 2H), 8.23-8.19 (m, 1H), 7.88 (td, *J* = 7.8, 1.2 Hz, 1H), 7.82 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55-7.51 (m, 1H), 7.38 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.23 (td, *J* = 7.8, 1.2 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.40 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.8, 154.6, 154.6, 142.5, 136.9, 133.9, 133.7, 130.8, 130.6, 130.1, 129.1, 128.2, 127.9, 127.6, 126.6, 125.6, 124.2, 122.1, 116.3, 110.0, 71.8, 27.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>23</sub>H<sub>15</sub>ClN<sub>3</sub>O<sub>3</sub><sup>+</sup>: 416.0796, found: 416.0802.

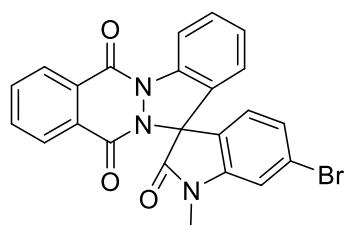
**1',5'-Dimethylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4j)**



**4j**

Product **4j** was isolated as a light yellow solid (34.0 mg, 43%); m.p. 280-282 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 7.8 Hz, 1H), 8.48-8.45 (m, 1H), 8.23-8.19 (m, 1H), 7.86 (td, *J* = 7.8, 1.2 Hz, 1H), 7.79 (td, *J* = 7.8, 1.2 Hz, 1H), 7.52-7.48 (m, 1H), 7.22-7.18 (m, 2H), 6.95-6.93 (m, 1H), 6.93-6.91 (m, 1H), 6.88 – 6.86 (m, 1H), 3.39 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.1, 154.6, 154.4, 141.5, 136.8, 133.7, 133.5, 133.4, 130.9, 130.4, 130.0, 128.4, 127.7, 127.6, 126.6, 126.5, 124.3, 122.1, 116.2, 108.7, 72.3, 27.1, 20.9. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>24</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>: 396.1343, found: 396.1352.

**6'-Bromo-1'-methylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4k)**

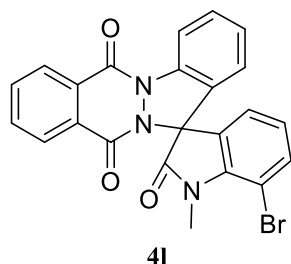


**4k**

Product **4k** was isolated as a light yellow solid (36.8 mg, 40%); m.p. 292-293 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51-8.44 (m, 2H), 8.22-8.17 (m, 1H), 7.88 (td, *J* = 7.8, 1.2 Hz, 1H), 7.81 (td, *J* = 7.68, 1.2 Hz, 1H), 7.54-7.49 (m, 1H), 7.22 (td, *J* = 7.8, 1.2 Hz, 1H), 7.20-7.17 (m, 2H), 6.96-6.90 (m, 2H), 3.39 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.0, 154.6, 145.3, 136.9, 133.9, 133.7, 130.8, 130.0, 128.2, 127.9, 127.61, 126.6, 125.7, 125.5, 125.0, 124.5, 122.1, 116.3, 112.61, 71.7, 27.3. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>23</sub>H<sub>15</sub>BrN<sub>3</sub>O<sub>3</sub><sup>+</sup>: 460.0291, found: 460.0291.

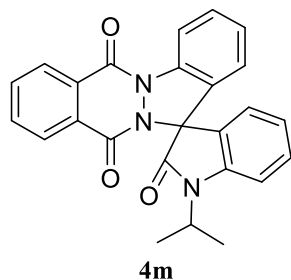
**7'-Bromo-1'-methylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione**

**e (4l)**



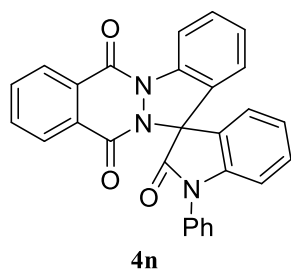
Product **4l** was isolated as a light yellow solid (29.5 mg, 32%); m.p. 286-287 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51-8.45 (m, 2H), 8.24-8.18 (m, 1H), 7.88 (td, *J* = 7.8, 1.2 Hz, 1H), 7.82 (td, *J* = 7.8, 1.2 Hz, 1H), 7.55-7.48 (m, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.01-6.94 (m, 2H), 6.90-6.85 (m, 1H), 3.79 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.8, 154.6, 154.5, 141.3, 136.8, 136.2, 133.9, 133.7, 130.7, 130.2, 129.8, 128.2, 127.9, 127.6, 126.6, 126.0, 124.8, 122.8, 122.1, 116.3, 103.4, 71.7, 30.9. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>23</sub>H<sub>15</sub>BrN<sub>3</sub>O<sub>3</sub><sup>+</sup>: 460.0291, found: 460.0301.

**1'-Isopropylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (4m)**



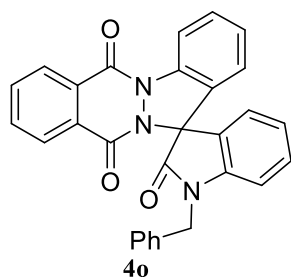
Product **4m** was isolated as a light yellow solid (45.0 mg, 55%); m.p. 291-293 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.49 (d, *J* = 8.4 Hz, 1H), 8.46 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.24-8.20 (m, 1H), 7.85 (td, *J* = 7.8, 1.2 Hz, 1H), 7.79 (td, *J* = 7.8, 1.2 Hz, 1H), 7.52-7.47 (m, 1H), 7.37 (td, *J* = 7.8, 1.2 Hz, 1H), 7.22-7.17 (m, 2H), 7.05 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.76-4.67 (m, 1H), 1.66-1.62 (m, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.83, 154.63, 154.38, 142.72, 136.86, 133.61, 133.48, 130.38, 130.28, 130.02, 128.50, 127.74, 127.67, 127.26, 126.80, 126.54, 123.91, 123.11, 121.86, 116.23, 110.52, 72.19, 45.26, 19.63, 19.16. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>25</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>: 410.1499, found: 410.1513.

### 1'-Phenylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (**4n**)



Product **4m** was isolated as a light yellow solid (26.6 mg, 30%); m.p. 246-248 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.4 Hz, 1H), 8.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87 (td, *J* = 7.8, 1.2 Hz, 1H), 7.81 (td, *J* = 7.8, 1.2 Hz, 1H), 7.63-7.60 (m, 2H), 7.59-7.56 (m, 2H), 7.55-7.51 (m, 1H), 7.48-7.44 (m, 1H), 7.32 (td, *J* = 7.8, 1.2 Hz, 1H), 7.26 (td, *J* = 7.8, 1.2 Hz, 1H), 7.13-7.09 (m, 2H), 7.06 (td, *J* = 7.8, 1.2 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 170.70, 154.68, 154.65, 144.31, 137.01, 134.33, 133.75, 133.59, 130.62, 130.52, 130.10, 129.80, 128.63, 128.46, 127.85, 127.71, 126.92, 126.63, 126.56, 126.44, 124.09, 123.98, 122.23, 116.30, 110.26, 72.35. HRMS (ESI) *m/z* calcd for [M+H]<sup>+</sup>: C<sub>28</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub><sup>+</sup>: 444.1343, found: 444.1355.

### 1'-benzylspiro[indazolo[1,2-*b*]phthalazine-13,3'-indoline]-2',6,11-trione (**4o**)



Product **4o** was isolated as a light yellow solid (37.5 mg, 41%); m.p. 251-253 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.51 (d, *J* = 8.4 Hz, 1H), 8.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.87 (td, *J* = 7.8, 1.2 Hz, 1H), 7.81 (td, *J* = 7.8, 1.2 Hz, 1H), 7.54-7.48 (m, 3H), 7.43-7.38 (m, 2H), 7.34-7.30 (m, 1H), 7.26 (td, *J* = 7.8, 1.2 Hz, 1H), 7.22 (td, *J* = 7.8, 1.2 Hz, 1H), 7.06 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.99 (td, *J* = 7.8, 1.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 171.3, 154.7, 154.5,

142.9, 136.9, 135.2, 133.7, 133.6, 130.5, 130.4, 130.1, 128.9, 128.4, 127.8, 127.8,  
127.7, 127.3, 126.8, 126.6, 126.6, 123.7, 123.6, 122.0, 116.3, 110.1, 72.2, 44.8.

HRMS (ESI)  $m/z$  calcd for  $[M+H]^+$ :  $C_{29}H_{20}N_3O_3^+$ : 458.1499, found: 458.1507.

## 7.2 Copies of NMR spectra

