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ORIGINAL PAPER

Highly efficient three-component synthesis of 1*H*-indazolo[1,2-*b*]phthalazinetrione derivatives catalyzed by heteropolyacids

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Abstract Efficient one-pot condensation of aldehyde, dimedone, and phthalhydrazide has been achieved in the presence of a catalytic amount of tungstosilicic acid under solvent-free conditions. A variety of 1*H*-indazolo-[1,2-*b*]phthalazinetrione derivatives were prepared in high to excellent yields in short time.

Keywords Multicomponent reaction · 1*H*-indazolo[1,2-*b*]phthalazinetrione · Aldehyde · Phthalhydrazide · Heteropolyacid · Solvent-free conditions

Introduction

Heterocycles containing the phthalazine ring are important targets in synthetic and medicinal chemistry, because this fragment is a key moiety in numerous biologically active compounds [1, 2]. Phthalazine derivatives, which have two bridgehead nitrogen atoms in a fused ring system, possess cytotoxic [3], antimicrobial [4], anticonvulsant [5], antifungal [6], anticancer [7], and anti-inflammatory [8] activities. Phthalazine-containing compounds are also highly potent inhibitors of vascular endothelial growth factor receptor II (VEGFR-2) [9–11]. Moreover, these compounds exhibited good promise as new luminescence materials or fluorescence probes [12]. In view of their great importance, several methods have been reported for synthesis of phthalazine derivatives, including the reaction of phthalhydrazide, aromatic aldehydes, and malononitrile [13, 14], the reaction of phthalhydrazide and dialkyl acetylenedicarboxylates in the presence of N-heterocycles [15], and palladium-catalyzed 1,3-dipolar cycloaddition of methylenecyclopropanes, vinylidenecyclopropane, and methylenecyclobutane with phthalhydrazide [16]. However, most of the reported procedures describe synthesis of only a narrow range of phthalazines. Thus, there is a need to develop general protocols for efficient preparation of heterocycles containing a phthalazine ring fragment.

In recent years, solid acids have found increased application in organic synthesis, as they may be easily recovered and recycled. Heteropolyacids (HPAs) are strong solid acids, harmless to the environment, and highly stable toward humidity, with flexibility in modifying acid strength [17]. Moreover, solvent-free reactions often provide clean, efficient, and high-yielding organic processes in heterocyclic synthesis [18]. As part of our continuing interest towards development of useful synthetic methodologies [19–23], we describe herein a simple synthesis of 1*H*-indazolo[1,2-*b*]phthalazinetriones by three-component condensation reaction of aldehyde, dimedone, and phthalhydrazide in the presence of a catalytic amount of tungstosilicic acid under solvent-free conditions (Scheme 1).

Results and discussion

Recently, we reported a method for synthesis of tetrahydrobenzo[*a*]xanthen-11-one derivatives promoted by heteropolyacids [24]. Keggin-type HPAs such as $H_3PW_{12}O_{40}$ (PWA), $H_3PMo_{12}O_{40}$ (PMoA), or $H_4SiW_{12}O_{40}$ (SiWA) are often employed as efficient and green catalysts in many organic transformations [25–29]. This prompted us to use these catalysts to survey the three-component reaction

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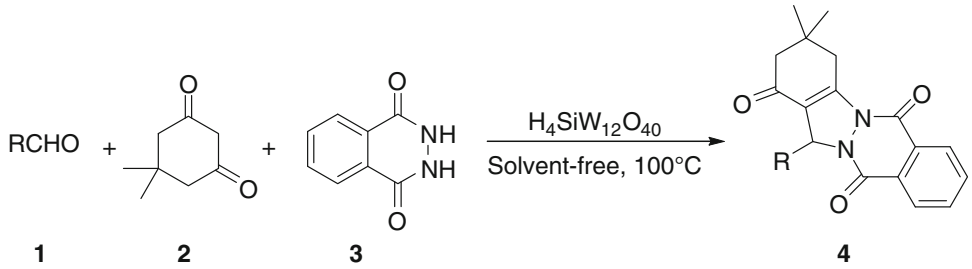
Scheme 1



of aldehyde, dimedone, and phthalhydrazide. A model reaction of 4-chlorobenzaldehyde, dimedone, and phthalhydrazide at 100 °C without catalyst under solvent-free conditions was performed in order to establish the true effectiveness of the catalyst. It was found that no conversion to 1*H*-indazolo[1,2-*b*]phthalazinetrione occurred even after 1 h of heating. When the reaction was performed in the presence of heteropolyacids, it proceeded mildly and rapidly to give the desired product in high yields. SiWA was found to be the most efficient catalyst compared with PWA and PMoA. The different activity between SiWA, PWA, and PMoA may be partially explained by a differing number of protons: four in SiWA, and three in PWA and PMoA [30]. Xia et al. [27] have investigated the intermolecular hydroamination of unactivated olefins with amides and benzyl carbamate catalyzed by heteropolyacids. Those authors noted that, in these cases, SiWA exhibited higher reactivity than PWA. Solid acids such as Dowex-50W, Amberlyst-15, montmorillonite K-10, montmorillonite KSF, $HClO_4$-SiO_2, and HBF_4-SiO_2 exhibited moderate to good catalytic properties, but all were inferior to SiWA. The use of HPA salts such as $(NH_4)_3PMo_{12}O_{40}$ was found to be far less effective (Table 1, entry 7). The catalytic activity of the recycled SiWA was also examined. When the reaction was completed, water was added and the product was filtered. The aqueous solution was evaporated under reduced pressure, and the obtained powder was washed with diethyl ether, dried, and reused for the same reaction again. It was observed that, with increasing number of cycles, the catalytic activity of the catalyst decreased slightly (Table 1, entry 10).

Next, the effect of temperature was evaluated for the model reaction. It was observed that the reaction did not proceed at room temperature. Elevating the reaction temperature proved helpful, and the yield of desired product **4j** increased considerably. We were pleased to find that the reaction proceeded smoothly, and almost complete conversion of product was observed at 100 °C, affording **4j** in 95% yield within shorter time. To compare the efficiency as well as capacity of the solvent-free conditions with respect to solution conditions, various solvents were examined. The results presented in Table 2 indicate that solvents affected the efficiency of the catalyst. Yields were lower in dichloromethane, ethanol, water, and polyethylene glycol (PEG). Better yields were obtained in ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) (Table 2, entries 7 and 8). However, the best result was obtained under solvent-free conditions (Table 2, entry 13). The effect of catalyst amount on the yield and rate was also investigated. It was found that 1 mol% of catalyst was sufficient, and excessive amounts of catalyst did not increase the yield remarkably.

Table 1 Influence of different catalysts on the reaction of 4-chlorobenzaldehyde, dimedone, and phthalhydrazide

Entry	Catalyst (mol%)	Time (min)	Yield (%)[a]
1	Dowex-50W (0.1 g)	30	62
2	Amberlyst-15 (0.1 g)	15	85
3	Montmorillonite K-10 (0.1 g)	30	65
4	Montmorillonite KSF (0.1 g)	30	70
5	$HClO_4$-SiO_2 (0.1 g)	15	87
6	HBF_4-SiO_2 (0.1 g)	30	85
7	$(NH_4)_3PMo_{12}O_{40}$ (1)	30	35
8	$H_3PMo_{12}O_{40}$ (1)	15	86
9	$H_3PW_{12}O_{40}$ (1)	10	85
10[b]	$H_4SiW_{12}O_{40}$ (1)	10	95, 93, 90, 89, 88, 85

Reaction conditions: 4-chlorobenzaldehyde (5 mmol), dimedone (5 mmol), and phthalhydrazide (5 mmol), 100 °C

[a] Yields refer to isolated pure products

[b] Catalyst was reused five times after drying

With this optimized procedure in hand, the scope of application of this three-component reaction was examined using different aldehydes as staring materials. As seen from Table 3, aromatic aldehydes having electron-donating as well as electron-withdrawing groups were uniformly transformed into the corresponding 1*H*-indazolo[1,2-*b*]phthalazinetriones in high to excellent yields within 10–25 min. Substituents on the aromatic ring had no obvious effect on yield or reaction time under the above optimal conditions. Inferior yield can generally be expected when less active aliphatic aldehydes such as cyclohexanecarbaldehyde and trichloroacetaldehyde (Table 3, entries **p**

Table 2 Optimization of reaction conditions

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (min)	Yield (%)[a]
1	1	CH_2Cl_2	Reflux	30	45
2	1	CH_3CN	Reflux	15	60
3	1	EtOH	Reflux	45	52
4	1	H_2O	Reflux	45	31
5	1	PEG 400	100	100	28
6	1	DMF	Reflux	35	40
7	1	[bmim][PF_6]	100	60	75
8	1	[bmim][BF_4]	100	60	68
9	1	No	r.t.	60	0
10	1	No	50	30	78
11	1	No	60	30	82
12	1	No	90	15	92
13	1	No	100	10	95
14	2	No	100	10	95
15	No	No	100	60	0

Reaction conditions: 4-chlorobenzaldehyde (5 mmol), dimedone (5 mmol), and phthalhydrazide (5 mmol)

[a] Yields are related to isolated pure products

Table 3 Preparation of 1*H*-indazolo[1,2-*b*] phthalazinetriones catalyzed by 12-tungstosilicic acid

Entry	Aldehydes **1**	Time (min)	Yield (%)[a]	R_f[b]	m.p. (°C)	
					Found	Lit.
a	Benzaldehyde	16	92	0.60	208–209	207–209 [34]
b	3-Methylbenzaldehyde	16	90	0.38	232–233	
c	4-Methylbenzaldehyde	15	91	0.30	227–228	226–228 [32]
d	3,4-Dimethylbenzaldehyde	15	89	0.36	250–251	
e	4-Methoxybenzaldehyde	15	90	0.25	218–220	218–220 [33]
f	3-Phenoxybenzaldehyde	25	91	0.38	188–189	
g	4-Fluorobenzaldehyde	20	83	0.29	220–222	217–219 [31]
h	2-Chlorobenzaldehyde	15	92	0.39	268–270	264–266 [32]
i	3-Chlorobenzaldehyde	20	93	0.35	205–206	204–206 [34]
j	4-Chlorobenzaldehyde	10	95	0.30	263–264	262–264 [31]
k	2,4-Dichlorobenzaldehyde	10	89	0.32	217–218	219–221 [34]
l	3-Bromobenzaldehyde	15	93	0.36	224–226	
m	4-Bromobenzaldehyde	20	90	0.36	266–268	265–267 [31]
n	3-Nitrobenzaldehyde	20	85	0.20	271–272	270–272 [34]
o	3-(Trifluoromethyl)benzaldehyde	13	85	0.28	213–215	
p	Cyclohexanecarbaldehyde	60	65	0.50	221–222	
q	Trichloroacetaldehyde	60	60	0.70	255–257	

[a] Yields refer to isolated products

[b] R_f values were examined by thin-layer chromatography (TLC) with a 1:1 mixture of ethylacetate:hexane as the solvent system

and **q**) were used as substrate, and incomplete conversion of the starting materials to the product was observed.

To compare the advantage of the use of SiWA over the reported procedure, the reaction of 4-chlorobenzaldehyde, dimedone, and phthalhydrazide was considered as a representative example (Table 4). While in most of these cases comparative yields of the desired product were obtained following the SiWA-catalyzed procedure, the reported procedures required high catalyst loading [31–35], long reaction time [33], and corrosive catalyst [33]. These results clearly demonstrate that SiWA is an equally or more efficient catalyst for this three-component reaction.

In order to elucidate the reaction mechanism, we also conducted the reaction of 2-(4-chlorobenzylidene)-5,5-dimethylcyclohexane-1,3-dione (**5**) [36] with phthalhydrazide in the presence of SiWA under the same conditions. Interestingly, **4j** was obtained in high yield (Scheme 2). It is reported that, in the absence of phthalhydrazide, the HPA-catalyzed reaction of aldehydes and dimedone resulted in the formation of xanthene derivatives as the reaction proceeds further after the condensation to give Michael products [37]. It is important to note that xanthene derivatives were not obtained in this three-component reaction. This is possibly due to the fast addition between **5**

Table 4 Comparison of SiWA with reported catalysts for the reaction of 4-chlorobenzaldehyde, dimedone, and phthalhydrazide

Catalyst/solvent/temperature (°C)	Catalyst load (mol%)	Time (min)	Yield (%)	Ref.
p-Toluenesulfonic acid/solvent-free/80	30	10	93	[31]
Silica sulfuric acid/solvent-free/100	6.5	7	91	[32]
H_2SO_4/[bmim][BF_4]/80	15	30	94	[33]
Poly phosphoric acid-SiO_2/solvent-free/100	5	6	93	[34]
$Mg(HSO_4)_2$/solvent-free/100	10	4	88	[35]
SiWA/solvent-free/100	1	10	95	This work

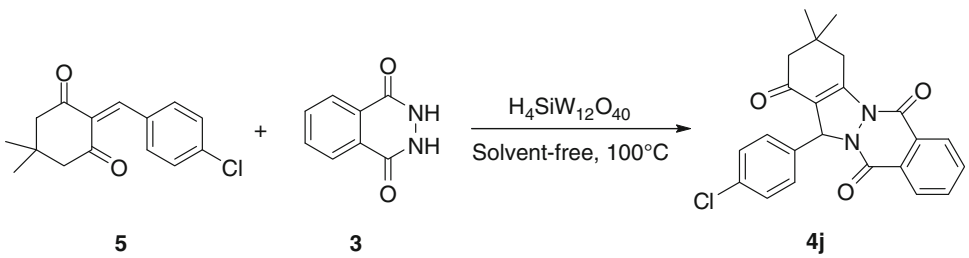
and phthalhydrazide. In addition, when we tried to react phthalhydrazide to **1j** or **2** using the above reaction conditions, a reaction did not proceed. On the basis of these findings, we propose a plausible mechanism for the reaction (Scheme 3). The reaction is thought to proceed in a stepwise manner. Firstly, we assume that the initial step is a Knoevenagel condensation between **1j** and **2**, resulting in adduct **5**, which suffers immediate Michael addition of phthalhydrazide to the C=C bond of **5**. The concerted cyclocondensation through amino and carbonyl of the Michael adduct **6** was performed to generate **4**. During the reaction process, the hydrogen ion is donated by the heteropolyacid. The hydrogen ion not only helps the dehydration but also benefits the enolization of dimedone to form the enolate intermediate. The isolated products **4** were racemic mixtures.

In conclusion, we have developed a highly efficient methodology for three-component reaction of aldehyde, dimedone, and phthalhydrazide catalyzed by cheap 12-tungstosilicic acid, furnishing a class of 1*H*-indazolo-[1,2-*b*]phthalazinetrione derivatives in high yield. This method is advantageous in terms of simplicity and mildness, and hopefully could find wide application in synthesis of complex phthalazine-containing compounds.

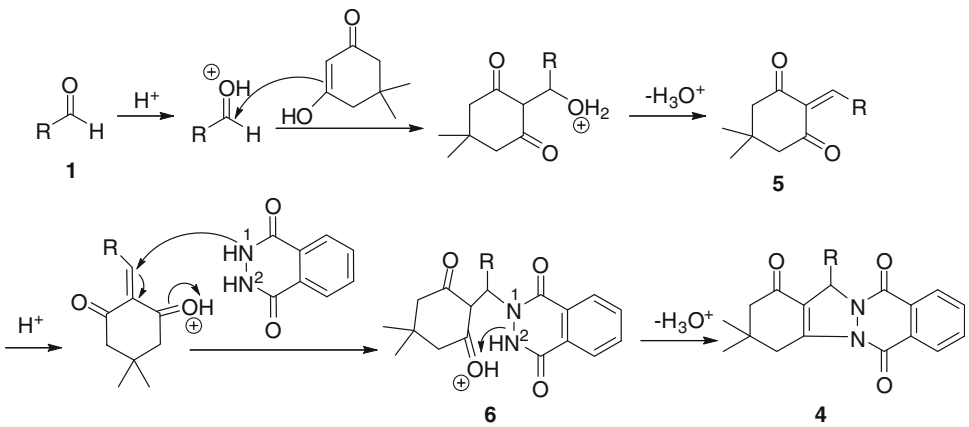
Experimental

Melting points were determined on an X-4 apparatus. Analytical thin-layer chromatography was performed on glass plates of silica gel GF_{254} of 0.2 mm thickness. Infrared (IR) spectra were obtained using a Shimadzu FTIR-8900 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DRX-500 spectrometer using tetramethylsilane (TMS) as internal standard. Mass spectra were performed on a ThermoFinnigan LCQ Advantage instrument with electrospray ionization (ESI, 4.5 keV) or Thermo Fisher Scientific

Scheme 2



Scheme 3



DSQ-II instrument with electron ionization (EI, 70 eV). Elemental analysis was carried out on a Vario EL III CHNOS elemental analyzer, and the results obtained agreed favorably with calculated values.

Representative procedure for synthesis of 1H-indazolo[1,2-b]phthalazinetrione derivatives

A mixture of 703 mg **1j** (5 mmol), 700 mg 5,5-dimethyl-1,3-cyclohexanedione (5.0 mmol), 820 mg **3** (5.0 mmol), and 143 mg $H_4SiW_{12}O_{40}$ (0.05 mmol) was heated at 100 °C. The reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and washed with water. The solid product was purified by recrystallization from aqueous EtOH to afford 1.93 g **4j** (95%).

The spectroscopic and physical data for known compounds **4a**, **4c**, **4e**, **4g**–**4k**, **4m**, and **4n** were found to be identical to those described in the literature [31–34].

2,3,4,13-Tetrahydro-3,3-dimethyl-13-(3-methylphenyl)-1H-indazolo[1,2-b]phthalazine-1,6,11-trione
(**4b**, $C_{24}H_{22}N_2O_3$)
Yellow needles, m.p.: 232–233 °C; IR (KBr): $\bar{\nu}$ = 1,639, 1,616, 1,419, 1,356, 1,315, 1,120, 1,066, 993, 952, 864 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.21 (s, 3H), 2.32 (s, 3H), 2.33 (s, 2H), 3.23 and 3.41 (AB system, J = 19.0 Hz, 2H), 6.40 (s, 1H), 7.08 (d, J = 7.5 Hz, 1H), 7.18–7.23 (m, 3H), 7.83–7.87 (m, 2H), 8.26–8.30 (m, 1H), 8.34–8.37 (m, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 21.5, 28.5, 28.6, 34.9, 38.1, 51.0, 65.0, 118.8, 124.1, 127.7, 127.9, 128.0, 128.6, 129.0, 129.2, 129.6, 133.4, 134.4, 136.3, 138.3, 150.7, 154.2, 156.1, 192.1 ppm; MS (EI): m/z = 386 (M^+, 12), 295 (100).

13-(3,4-Dimethylphenyl)-2,3,4,13-tetrahydro-3,3-dimethyl-1H-indazolo[1,2-b]phthalazine-1,6,11-trione
(**4d**, $C_{25}H_{24}N_2O_3$)
Yellow needles, m.p.: 250–251 °C; IR (KBr): $\bar{\nu}$ = 1,635, 1,616, 1,419, 1,357, 1,315, 1,263, 1,120, 1,066, 993, 952, 864 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.21 (s, 3H), 2.19 (s, 3H), 2.22 (s, 3H), 2.33 (s, 2H), 3.23 and 3.42 (AB system, J = 19.0 Hz, 2H), 6.38 (s, 1H), 7.07–7.17 (m, 3H), 7.82–7.86 (m, 2H), 8.26–8.28 (m, 1H), 8.33–8.36 (m, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 19.6, 19.9, 28.5, 28.7, 34.7, 38.1, 51.0, 64.9, 118.9, 124.5, 127.8, 127.9, 128.5, 129.0, 129.2, 130.0, 133.4, 133.7, 134.4, 136.9, 137.2, 150.7, 154.2, 156.1, 192.1 ppm; MS (EI): m/z = 400 (M^+, 63), 295 (100).

2,3,4,13-Tetrahydro-3,3-dimethyl-13-(3-phenoxyphenyl)-1H-indazolo[1,2-b]phthalazine-1,6,11-trione
(**4f**, $C_{29}H_{24}N_2O_4$)
Yellow powder, m.p.: 188–189 °C; IR (KBr): $\bar{\nu}$ = 1,635, 1,616, 1,452, 1,365, 1,311, 1,272, 1,240, 1,070, 985, 864 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): = 1.16 (s, 3H), 1.19 (s, 3H), 2.33 (s, 2H), 3.21 and 3.36 (AB system, J = 19.0 Hz, 2H), 6.41 (s, 1H), 6.88 (dd, J = 8.0, 2.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 7.01 (t, J = 2.0 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.27–7.31 (m, 3H), 7.83–7.88 (m, 2H), 8.27–8.30 (m, 1H), 8.33–8.36 (m, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 28.4, 28.7, 34.6, 38.0, 51.0, 64.6, 117.1, 118.3, 118.6, 119.1, 122.4, 123.4, 127.8, 128.0, 129.0, 129.1, 129.7, 129.9, 133.6, 134.6, 138.4, 151.0, 154.4, 156.0, 156.7, 157.6, 192.1 ppm; MS (ESI): m/z = 465 (M + 1)$^+$.

13-(3-Bromophenyl)-2,3,4,13-tetrahydro-3,3-dimethyl-1H-indazolo[1,2-b]phthalazine-1,6,11-trione
(**4l**, $C_{23}H_{19}BrN_2O_3$)
Yellow powder, m.p.: 224–226 °C; IR (KBr): $\bar{\nu}$ = 1,635, 1,618, 1,458, 1,419, 1,363, 1,309, 1,265, 1,120, 1,068, 952, 864 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.20 (s, 3H), 1.21 (s, 3H), 2.34 (s, 2H), 3.24 and 3.41 (AB system, J = 19.0 Hz, 2H), 6.39 (s, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 2.0 Hz, 1H), 7.85-7.89 (m, 2H), 8.26–8.29 (m, 1H), 8.35–8.38 (m, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 28.5, 28.6, 34.7, 38.0, 50.9, 64.3, 117.1, 122.8, 126.4, 127.8, 128.1, 129.0, 129.8, 130.2, 131.9, 133.7, 134.6, 138.7, 151.2, 154.4, 156.0, 192.0 ppm; MS (ESI): m/z = 452 (M + 1)$^+$.

2,3,4,13-Tetrahydro-3,3-dimethyl-13-[3-(trifluoromethyl)phenyl]-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (**4o**, $C_{24}H_{19}F_3N_2O_3$)
Yellow needles, m.p.: 213–215 °C; IR (KBr): $\bar{\nu}$ = 1,635, 1,616, 1,359, 1,311, 1,263, 1,078, 983, 864 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.21 (s, 3H), 1.22 (s, 3H), 2.34 (s, 2H), 3.24 and 3.43 (AB system, J = 19.0 Hz, 2H), 6.49 (s, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.60 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.85–7.89 (m, 2H), 8.25–8.28 (m, 1H), 8.36–8.39 (m, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 28.3, 28.8, 34.7, 38.1, 50.9, 64.3, 117.1, 123.5, 123.6 (q, J = 3.7 Hz), 125.6 (q, J = 3.6 Hz), 126.5 (q, J = 270.8 Hz), 127.8, 128.2, 128.9, 129.0, 129.2, 131.1, 131.2 (q, J = 37.5 Hz), 133.8, 134.7, 137.5, 151.4, 154.6, 156.1, 192.1 ppm; MS (EI): m/z = 440 (M^+, 45), 295 (100).

13-Cyclohexyl-2,3,4,13-tetrahydro-3,3-dimethyl-1H-indazolo[1,2-b]phthalazine-1,6,11-trione (**4p**, $C_{23}H_{26}N_2O_3$)
Yellow powder, m.p.: 221–222 °C; IR (KBr): $\bar{\nu}$ = 2,929, 2,853, 1,661, 1,469, 1,375, 1,361, 1,330, 1,269, 1,148,

697 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.03$–1.24 (m, 11H), 1.59–1.78 (s, 6H), 2.28 (d, $J = 9.0$ Hz, 1H), 2.33 and 2.43 (AB system, $J = 16.5$ Hz, 2H), 3.07 and 3.35 (AB system, $J = 19.0$ Hz, 2H), 7.85 (t, $J = 7.5$ Hz, 1H), 7.90 (t, $J = 7.5$ Hz, 1H), 8.32 (d, $J = 7.5$ Hz, 1H), 8.36 (d, $J = 7.5$ Hz, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 26.1$, 26.2, 26.3, 28.5, 28.7, 29.3, 34.3, 38.0, 41.4, 51.2, 66.8, 117.3, 127.7, 127.9, 128.9, 129.2, 133.4, 134.5, 152.2, 155.2, 156.1, 193.0 ppm; MS (ESI): $m/z = 379$ $(M + 1)^+$.

2,3,4,13-Tetrahydro-3,3-dimethyl-13-trichloromethyl-1H-indazolo[1,2-b]phthalazine-1,6,11-trione
(**4q**, $C_{18}H_{15}Cl_3N_2O_3$)
Pale yellow powder, m.p.: 255–257 °C; IR (KBr): $\bar{v} = 2{,}957$, 1,678, 1,613, 1,463, 1,410, 1,391, 1,377, 1,316, 1,256, 1,147, 1,125, 822, 696 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.18$ (s, 3H), 1.28 (s, 3H), 2.30 and 2.50 (AB system, $J = 16.5$ Hz, 2H), 2.99 and 3.42 (AB system, $J = 19.5$ Hz, 2H), 6.56 (s, 1H), 7.89 (t, $J = 7.5$ Hz, 1H), 7.93 (t, $J = 7.5$ Hz, 1H), 8.33 (d, $J = 7.5$ Hz, 1H), 8.36 (d, $J = 7.5$ Hz, 1H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 27.9$, 29.1, 34.0, 37.8, 51.1, 70.7, 100.9, 113.6, 128.4, 128.5, 128.6, 128.7, 134.2, 135.1, 156.3, 156.4, 157.6, 190.9 ppm; MS (ESI): $m/z = 414$ $(M + 1)^+$.

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